

## Supporting Information

### **Observation by NMR of cationic Wheland-like intermediates in the deiodination of protected 1-iodonaphthalene-2,4-diamines in acidic media**

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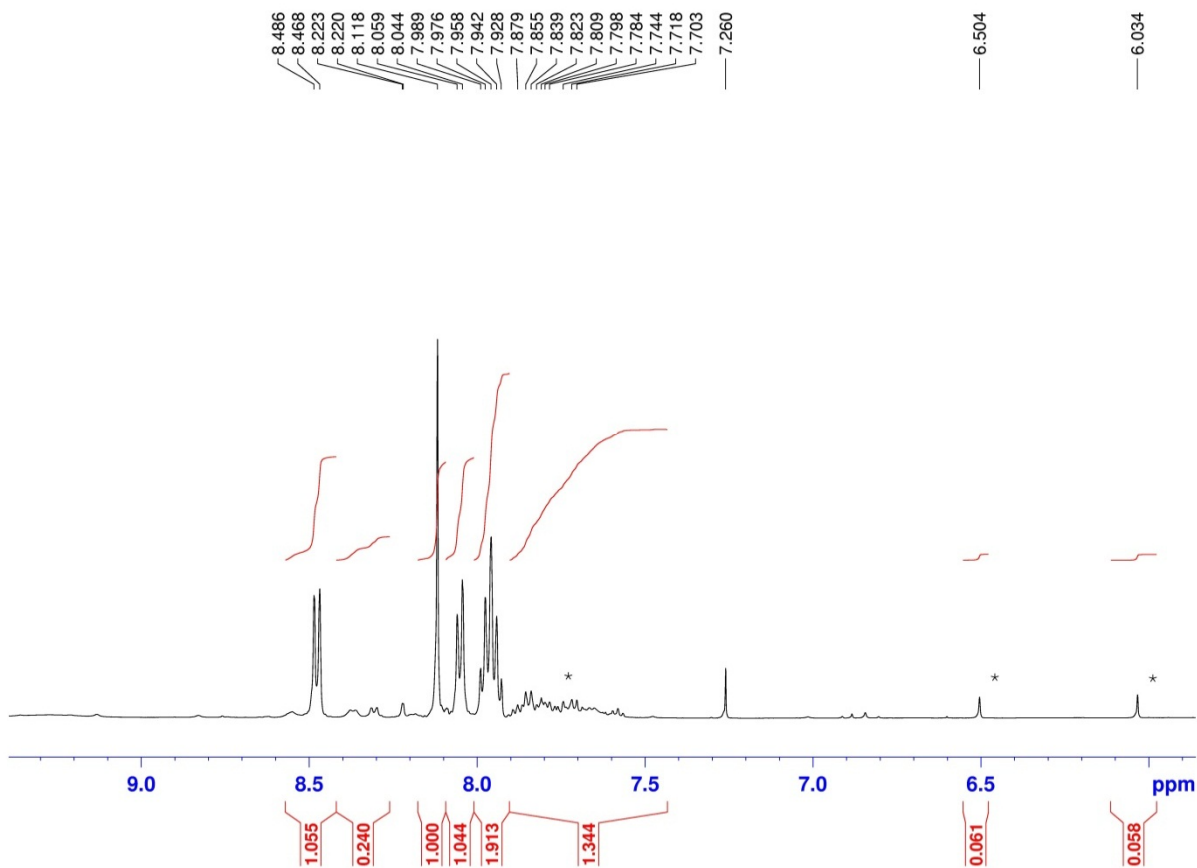
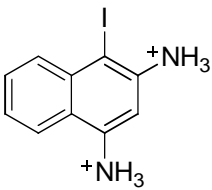
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*In the Supplementary Information, the numbering of the positions on the naphthalene rings follows strict IUPAC numbering.*

**Reactions monitored by NMR.**

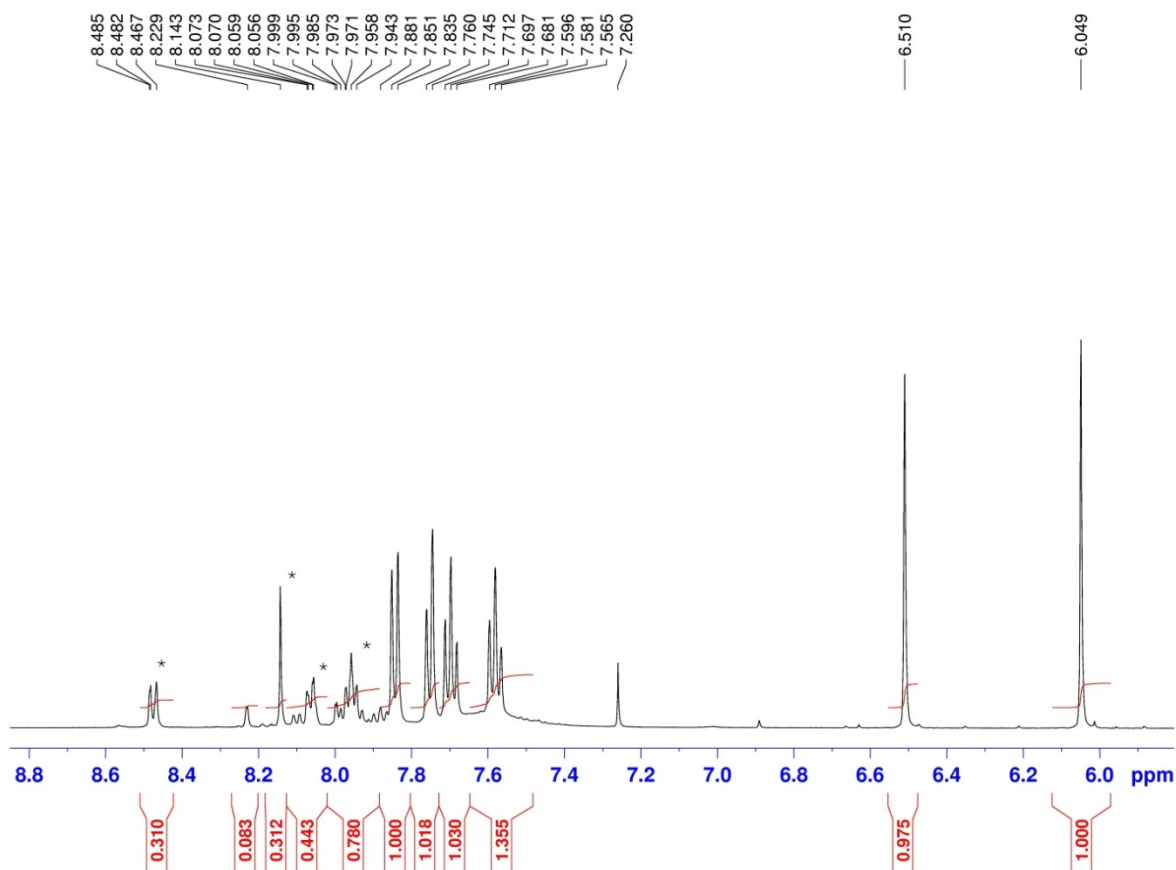
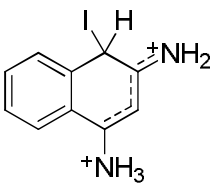
In a typical reaction, **11** (14.0 mg, 0.29 mmol) was dissolved in a mixture of CDCl<sub>3</sub> (0.15 mL) and trifluoroacetic acid (CF<sub>3</sub>CO<sub>2</sub>D or CF<sub>3</sub>CO<sub>2</sub>H) (0.45 mL) at 0°C. Following brief agitation of the sample with a vortex mixer to ensure dissolution and homogeneity of the sample, it was transferred to the NMR spectrometer, with the probe pre-cooled to 0°C. Following locking and shimming, data could be collected, typically within 3-4 minutes of mixing the sample. Where samples were monitored for extended times (days / weeks), the samples were stored in a laboratory which was regulated to 20 ± 1°C.

**15**: <sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H), 500.13 MHz, 273 K) δ 7.93-8.01 (2 H, m, 6,7-H<sub>2</sub>), 8.05 (1 H, d, *J* 8.0 Hz, 5-H), 8.11 (1 H, s, 3-H), 8.42 (1 H, d, *J* 8.5 Hz, 8-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/ CF<sub>3</sub>CO<sub>2</sub>H, 125.77 MHz, 293 K) δ 101.44 (1-C), 116.90 (3-C), 120.96 (5-C), 126.61 (4a-C), 127.75 (4-C), 129.38 (2-C), 131.81 (6-C), 132.34 (7-C), 134.72 (8-C), 135.96 (8a-C).

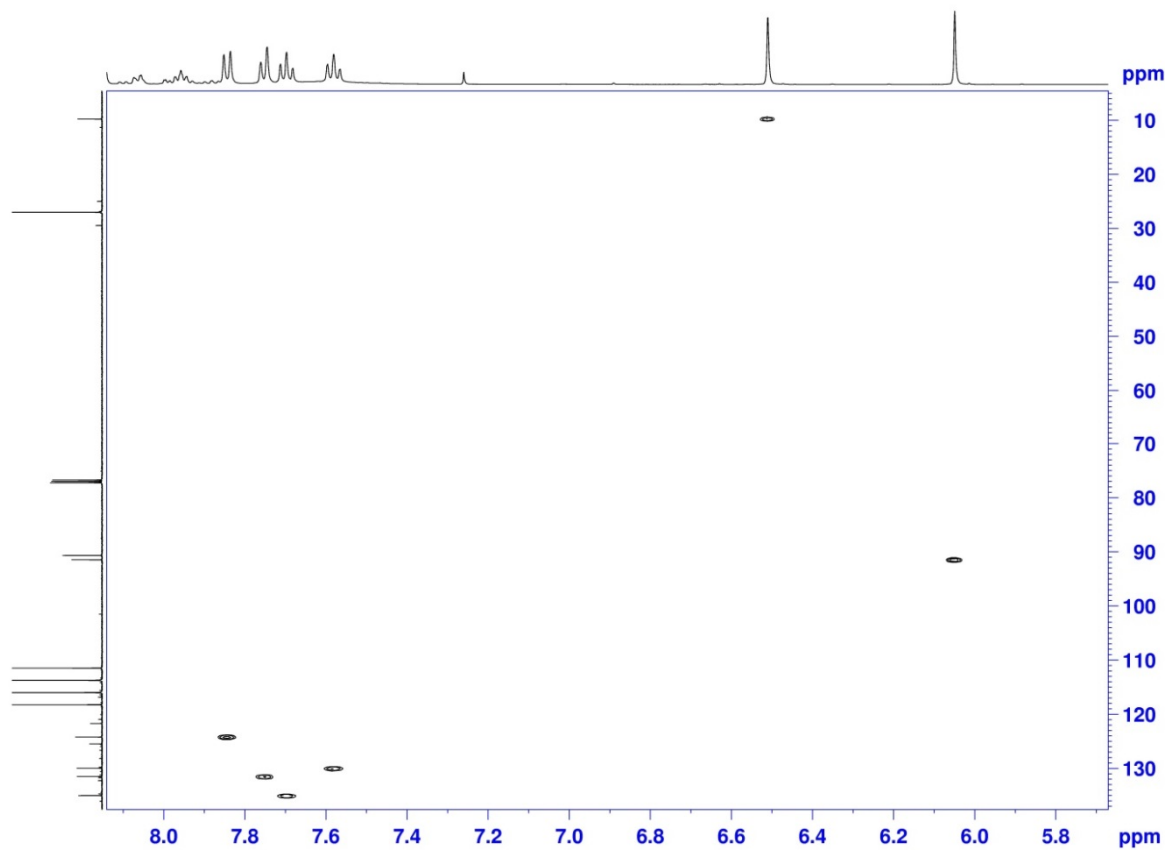


**Figure 1.** <sup>1</sup>H NMR spectrum of **15** at 0°C, showing small amounts of **11** (\*) formed.

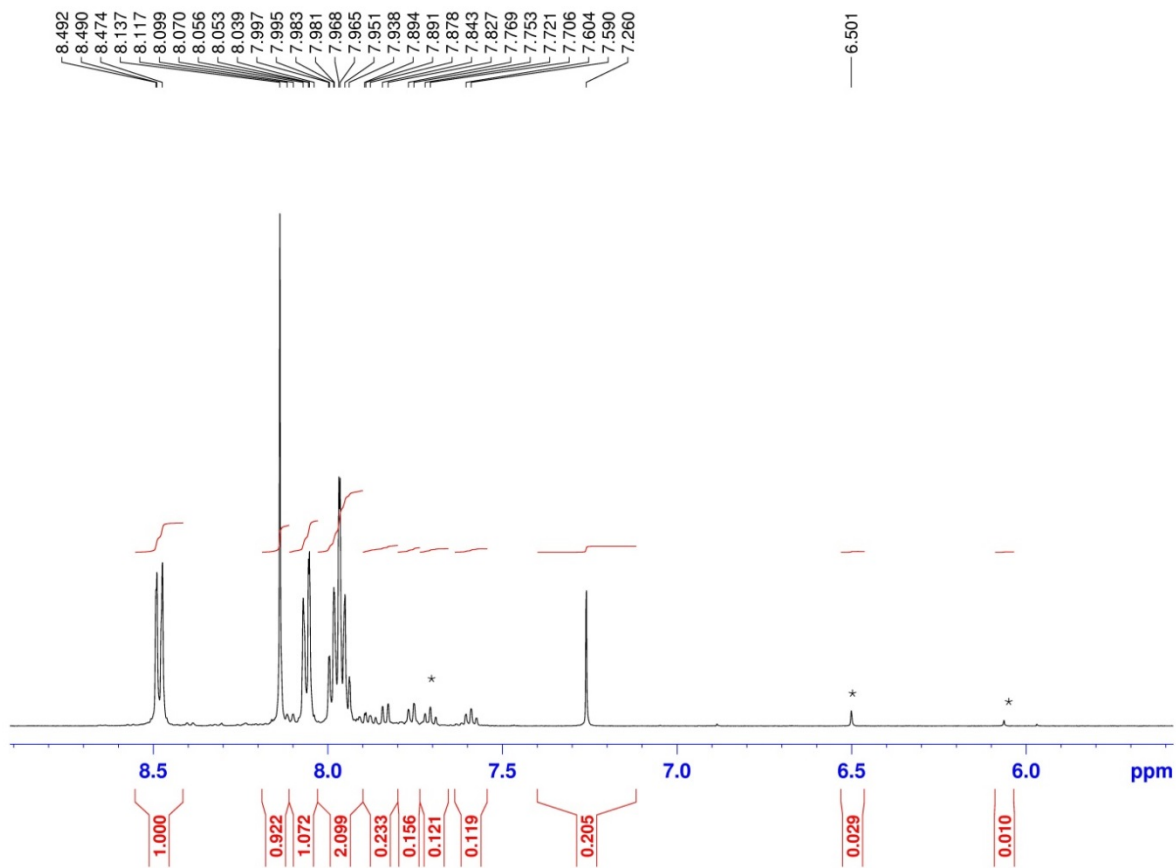
**16:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 500.13 MHz, 293 K)  $\delta$  6.05 (1 H, s, 3-H), 6.51 (1 H, s, 1-H), 7.58 (1 H, t,  $J$  7.8 Hz, 6-H), 7.70 (1 H, t,  $J$  7.8 Hz, 7-H), 7.75 (1 H, d,  $J$  7.8 Hz, 8-H), 7.84 (1 H, d,  $J$  8.0 Hz, 5-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 125.77 MHz, 293 K)  $\delta$  9.79 (1-C), 91.49 (3-C), 121.68 (4a-C), 124.16 (5-C), 129.93 (6-C), 131.48 (8-C), 135.01 (7-C), 141.25 (8a-C), 164.30 (4-C), 173.50 (2-C).



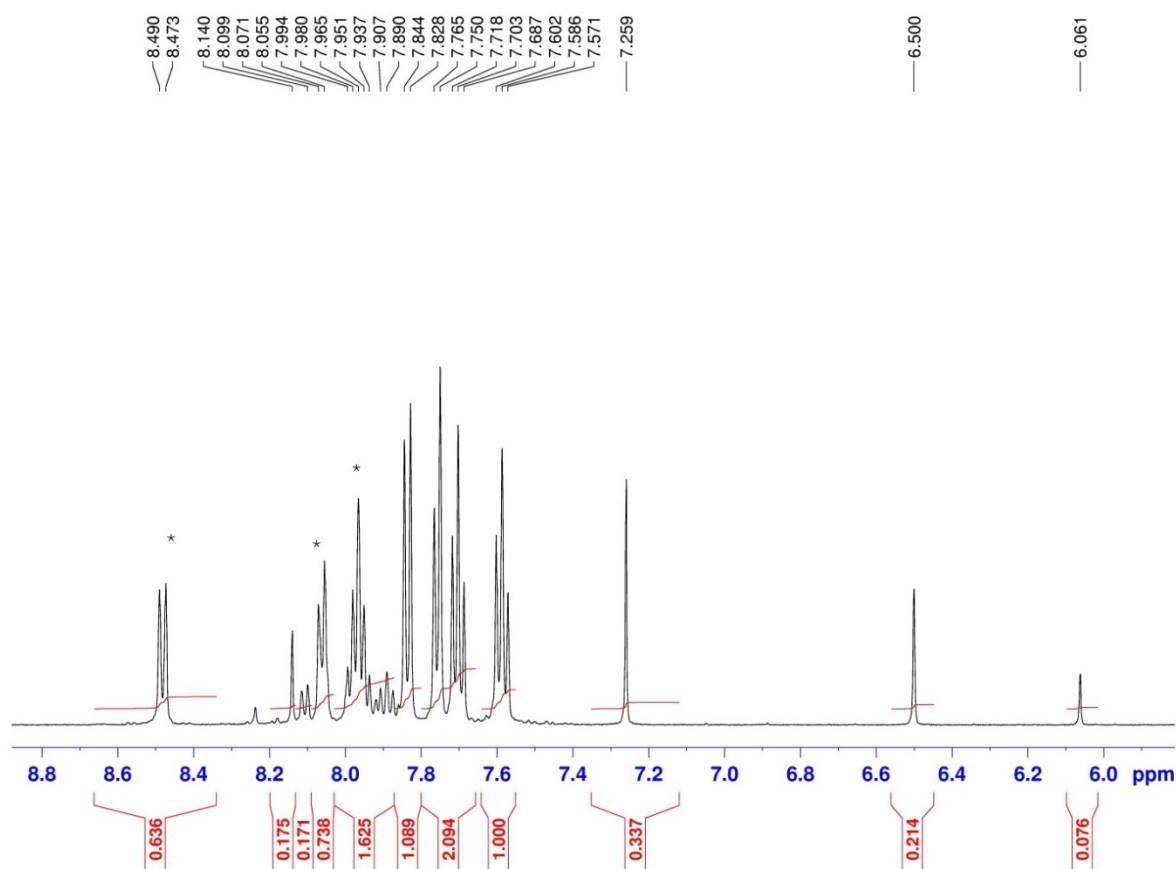
**Figure 2.**  $^1\text{H}$  NMR spectrum of **16** at 20°C, showing small residual amounts of **10** (\*).



**Figure 3.** HSQC NMR spectrum of **16** at 20°C, showing the peak for CHI at  $\delta$  6.50 ( $^1\text{H}$ ) and  $\delta$  9.54 ( $^{13}\text{C}$ ).

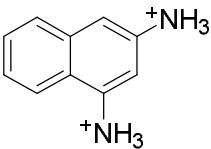


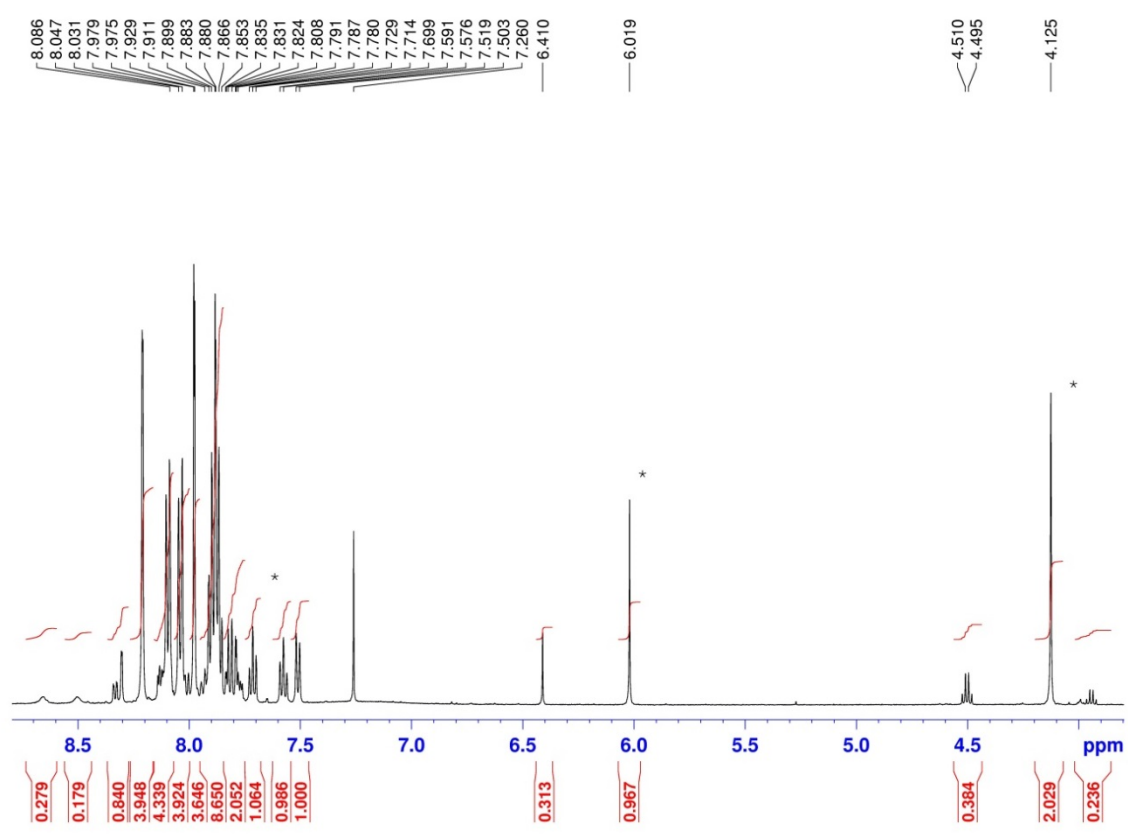
**Figure 4.**  $^1\text{H}$  NMR spectrum of **17** with traces of **18** (\*), following reaction of **11** with  $\text{CF}_3\text{CO}_2\text{D}$  /  $\text{CDCl}_3$  at 0°C.



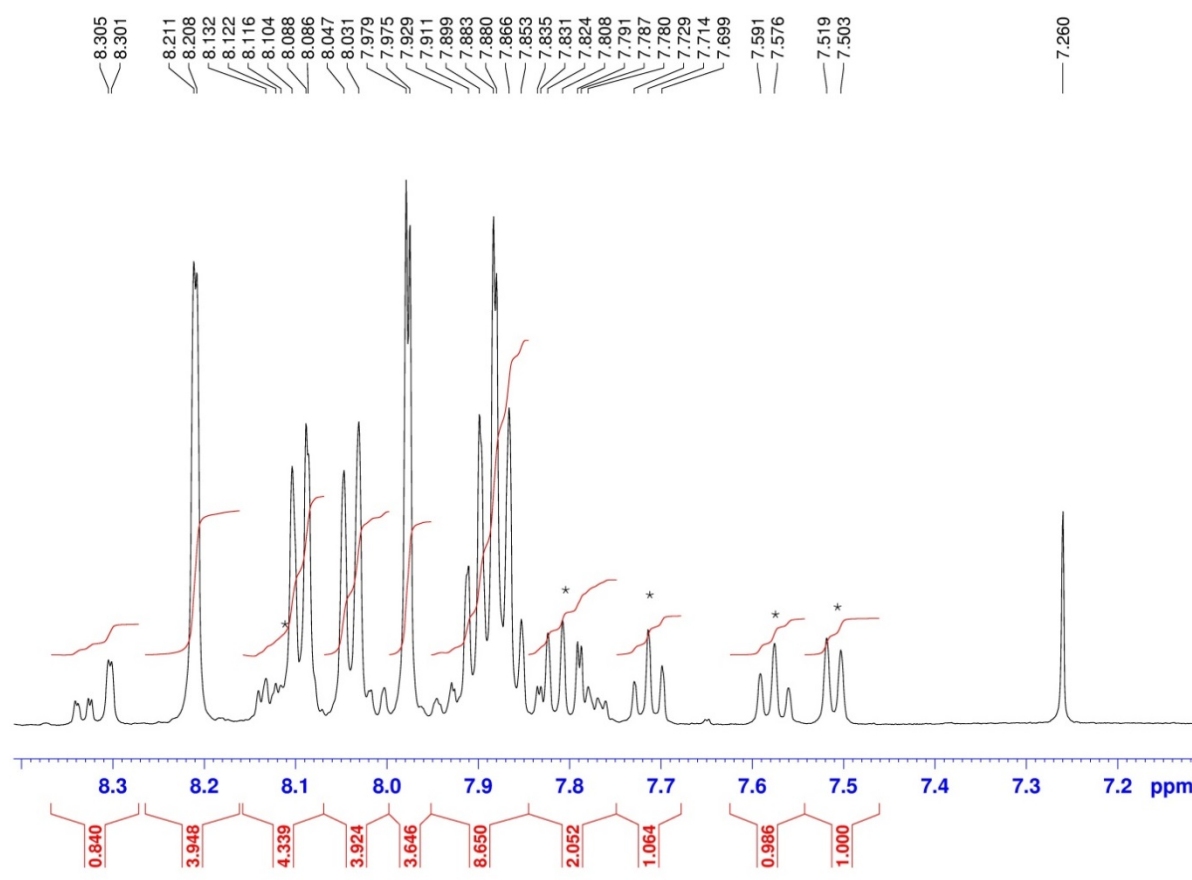
**Figure 5.**  $^1\text{H}$  NMR spectrum of **18** with traces of **17** (\*), following reaction of **11** with  $\text{CF}_3\text{CO}_2\text{D}$  /  $\text{CDCl}_3$  at  $20^\circ\text{C}$ . Note the reduced intensity of the peaks at  $\delta$  6.50 and  $\delta$  6.08 where deuterium has exchanged in the Wheland-type molecule and the peak at  $\delta$  8.14 showing that deuterium is present in **17**.

**20:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 500.13 MHz, 293 K)  $\delta$  7.88-7.99 (2 H, m, 6,7- $\text{H}_2$ ), 8.05 (1 H, s, 2-H), 8.10 (1 H, d,  $J$  8.2 Hz, 8-H), 8.14 (1 H, d,  $J$  7.7 Hz, 5-H), 8.28 (1 H, s, 1-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 125.77 MHz, 293 K)  $\delta$  116.62 (2-C), 120.05 (8-C), 125.19 (3-C), 126.05 (4-C), 126.73 (4a-C), 129.87 (5-C), 130.57 (6-C), 131.27 (7-C), 134.29 (1-C), 134.33 (3-C).

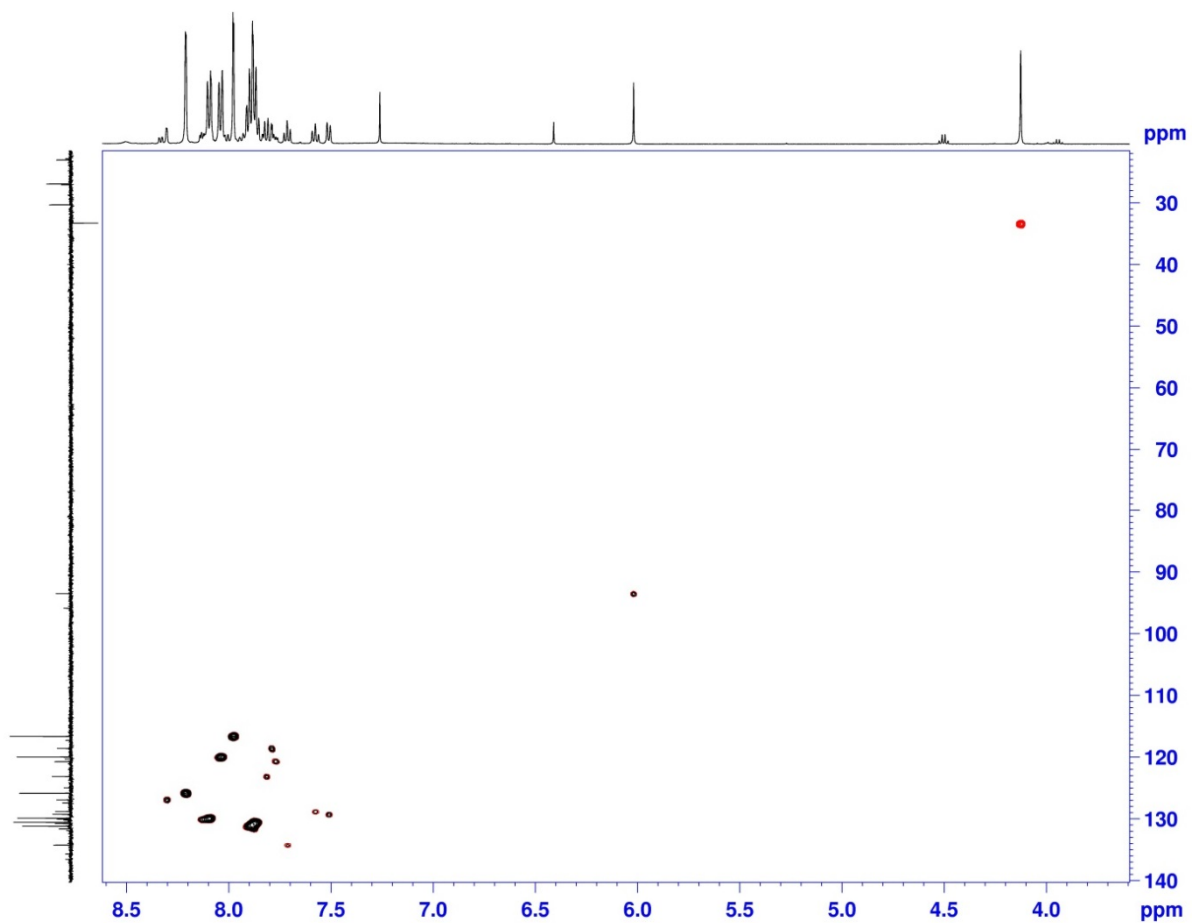




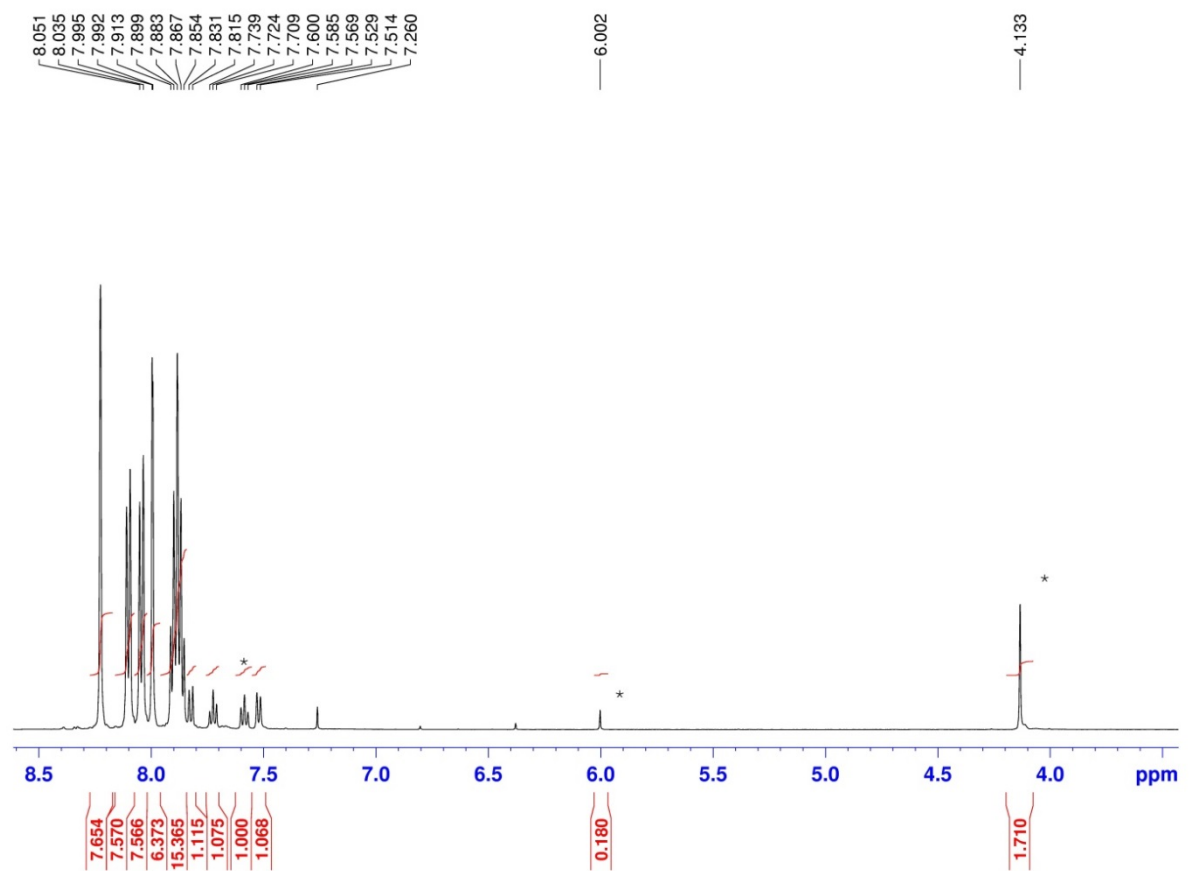
**Figure 6.** <sup>1</sup>H NMR spectrum of **20** and **21** (\*) shortly after dissolution of **9** in CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>D at 0°C.



**Figure 7.** Expansion of Figure 6 to show aromatic region in more detail.



**Figure 8.** HSQC NMR spectrum of **20** and **21** showing CH<sub>2</sub> of the Wheland-type species at  $\delta$  4.13 (<sup>1</sup>H) and  $\delta$  33.27 (<sup>13</sup>C).



**Figure 9.** <sup>1</sup>H NMR spectrum of **22** and **23** (\*) shortly after dissolution of **4** in CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>D at 0°C.

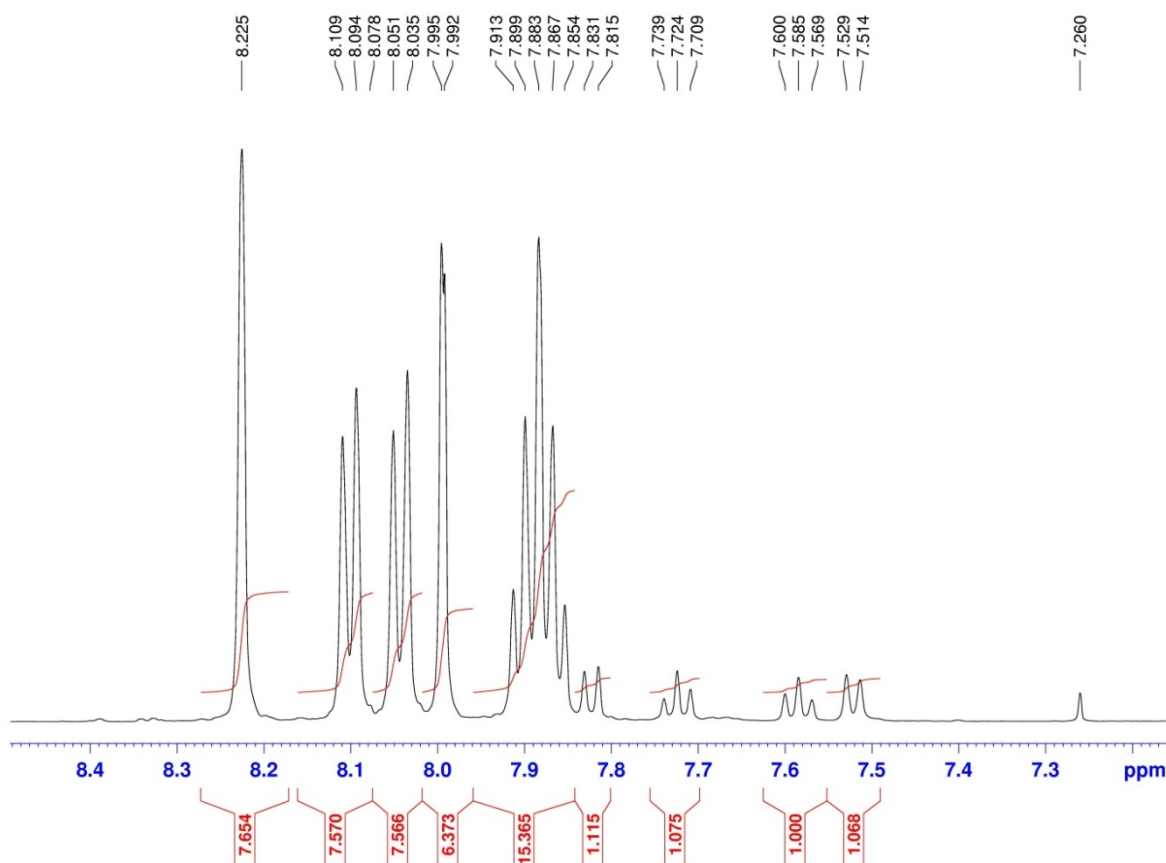


Figure 10. Expansion of Figure 9 to show aromatic region.

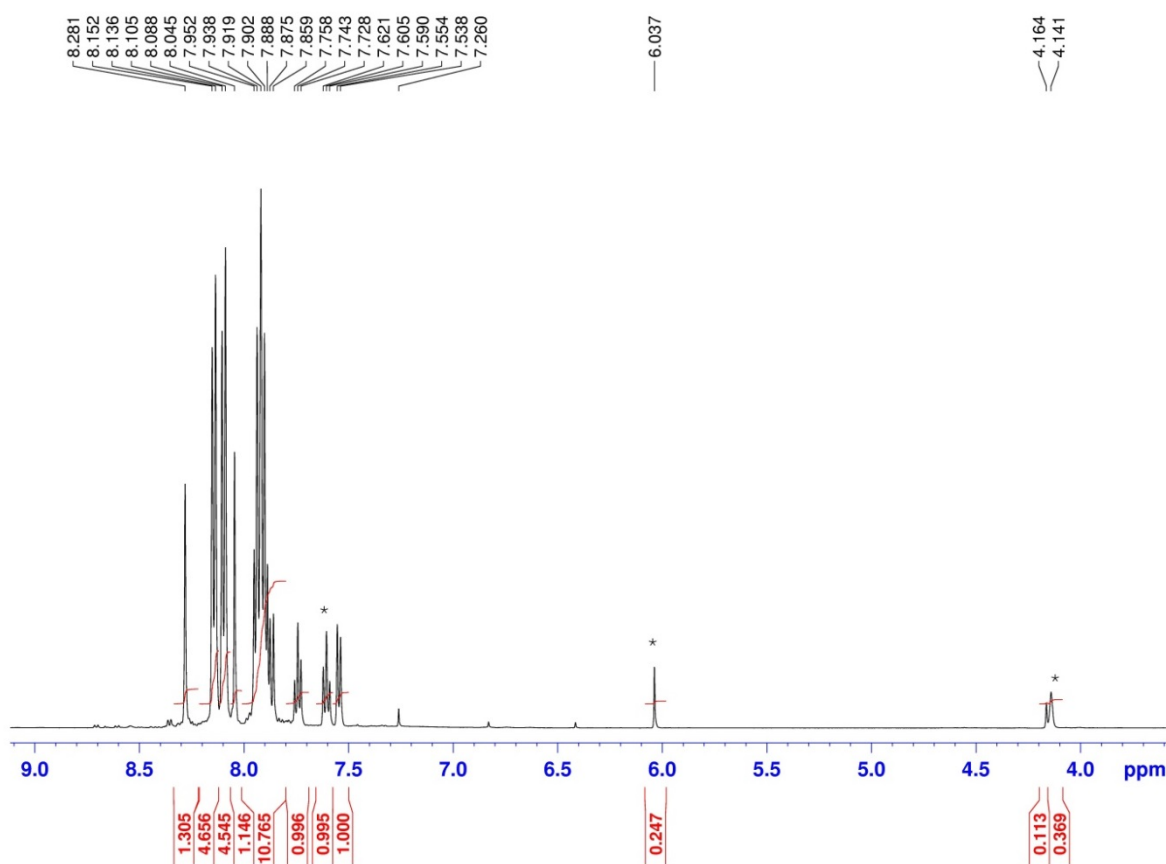
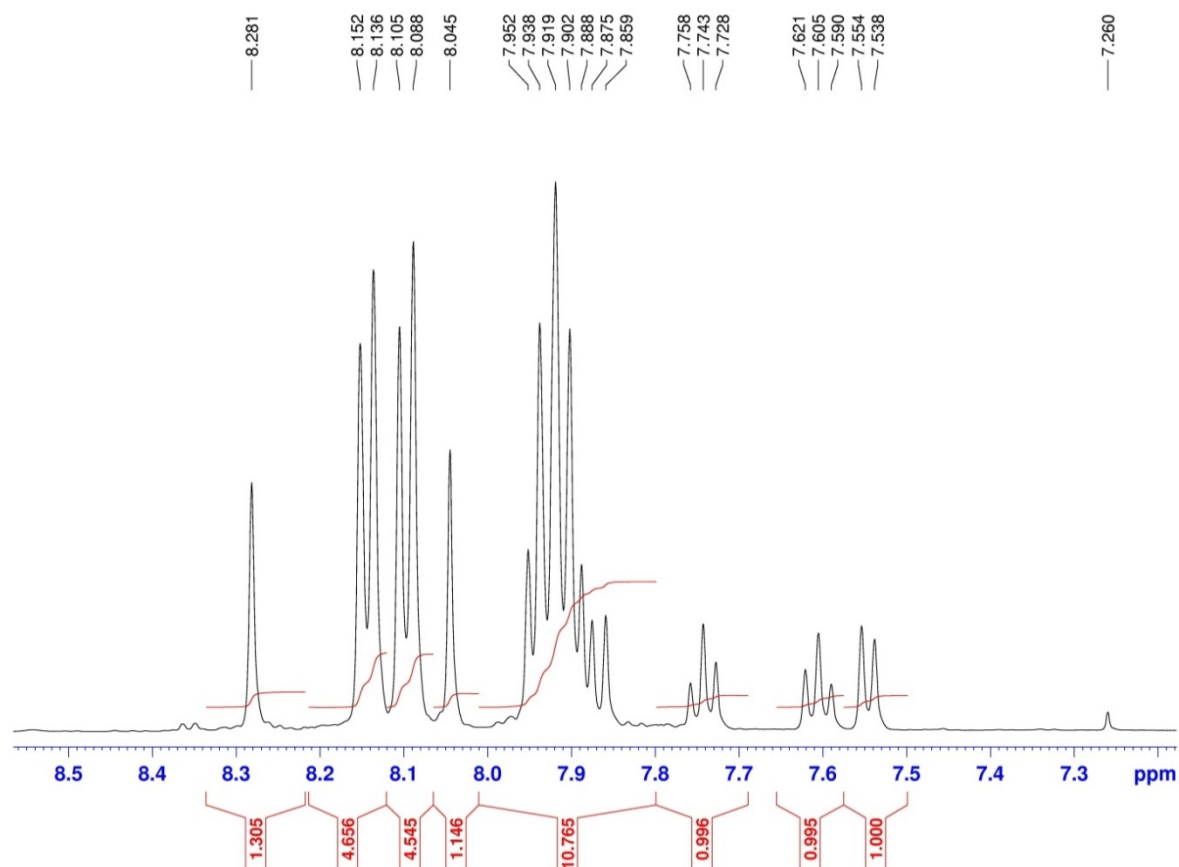
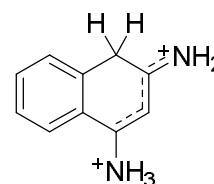


Figure 11. <sup>1</sup>H NMR spectrum of **22** and **23** (\*) 48 h after dissolution of **9** in CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>D.

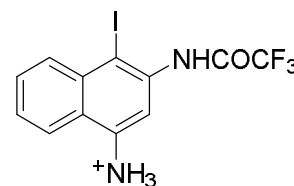


**Figure 12.**  $^1\text{H}$  expansion of Figure 11 to show aromatic region. Note the diminished intensity of the singlets at  $\delta$  8.28 and  $\delta$  8.05 due to exchange of H with D at 1-H and 3-H in **22**.

**21:**  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 500.13 MHz, 293 K)  $\delta$  4.13 (2 H, s, 4- $\text{H}_2$ ), 6.01 (1 H, s, 2-H), 7.55 (1 H, d,  $J$  7.9 Hz, 5-H), 7.61 (1 H, t,  $J$  7.5 Hz, 7-H), 7.74 (1 H, t,  $J$  7.5 Hz, 6-H), 7.87 (1 H, d,  $J$  7.9 Hz, 8-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 125.77 MHz, 293 K)  $\delta$  33.27 (4-C), 93.58 (2-C), 123.02 (8a-C), 123.22 (8-C), 128.85 (7-C), 129.29 (5-C), 134.31 (6-C), 136.52 (4a-C), 165.73 (1-C), 171.87 (3-C).



**27:**  $^1\text{H}$  (500.13 MHz,  $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 273 K)  $\delta$  7.84 (1 H, t,  $J$  7.5 Hz, 6-H), 7.88 (1 H, t,  $J$  7.5 Hz, 1H, 7-H), 7.97 (1 H, d,  $J$  8.2 Hz, 5-H), 8.44 (1 H, d,  $J$  8.6 Hz, 8-H), 8.57 (1 H, s, 3-H);  $^{13}\text{C}$  NMR (125.77 MHz,  $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ , 273 K)  $\delta$  99.94 (1-C), 116.65 (q,  $J$  108.8 Hz,  $\text{CF}_3$ ), 116.71 (3-C), 120.59 (5-C), 125.48 (4a-C), 126.84 (4-C), 130.40 (6-C), 131.40 (7-C), 133.71 (2-C), 134.58 (8-C), 135.68 (8a-C), 158.24 (q,  $J$  40.3 Hz, C=O).



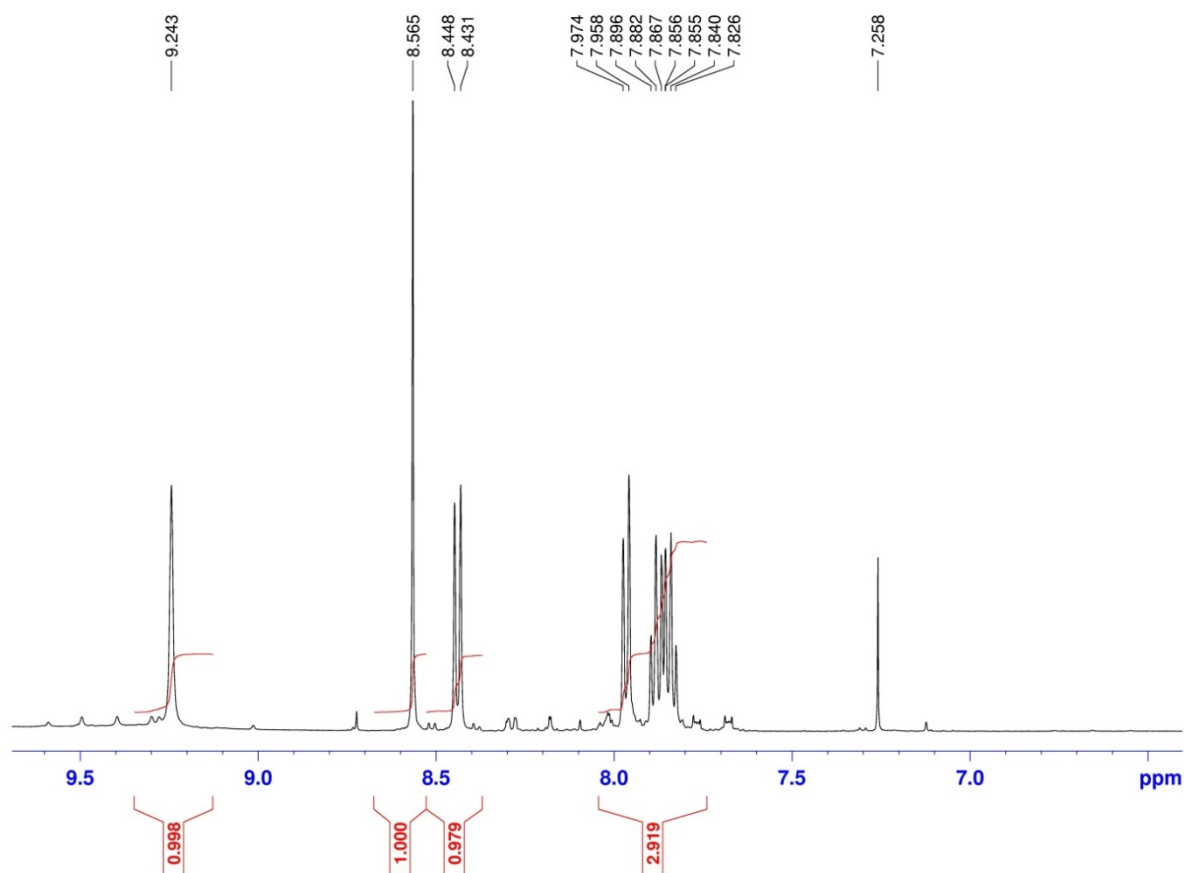


Figure 13. <sup>1</sup>H NMR spectrum of **27** in CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>D.

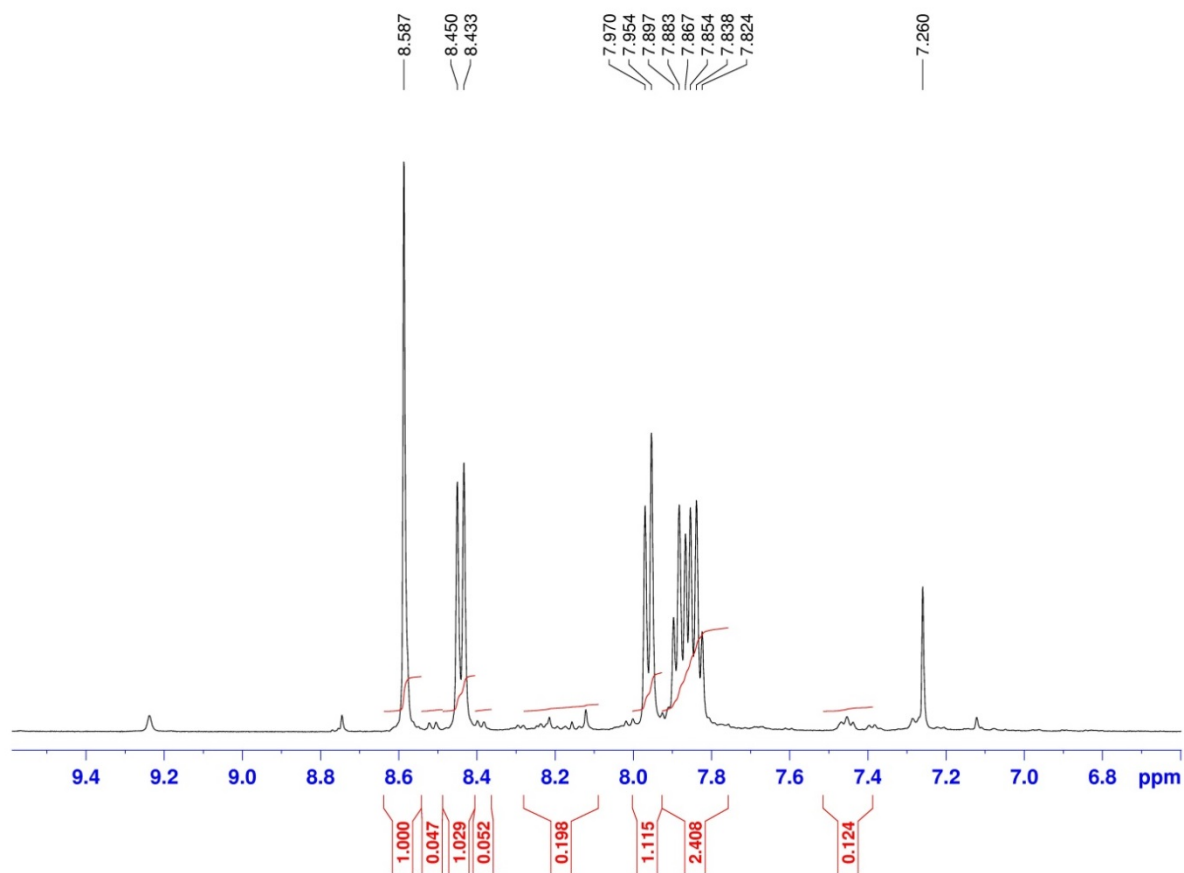
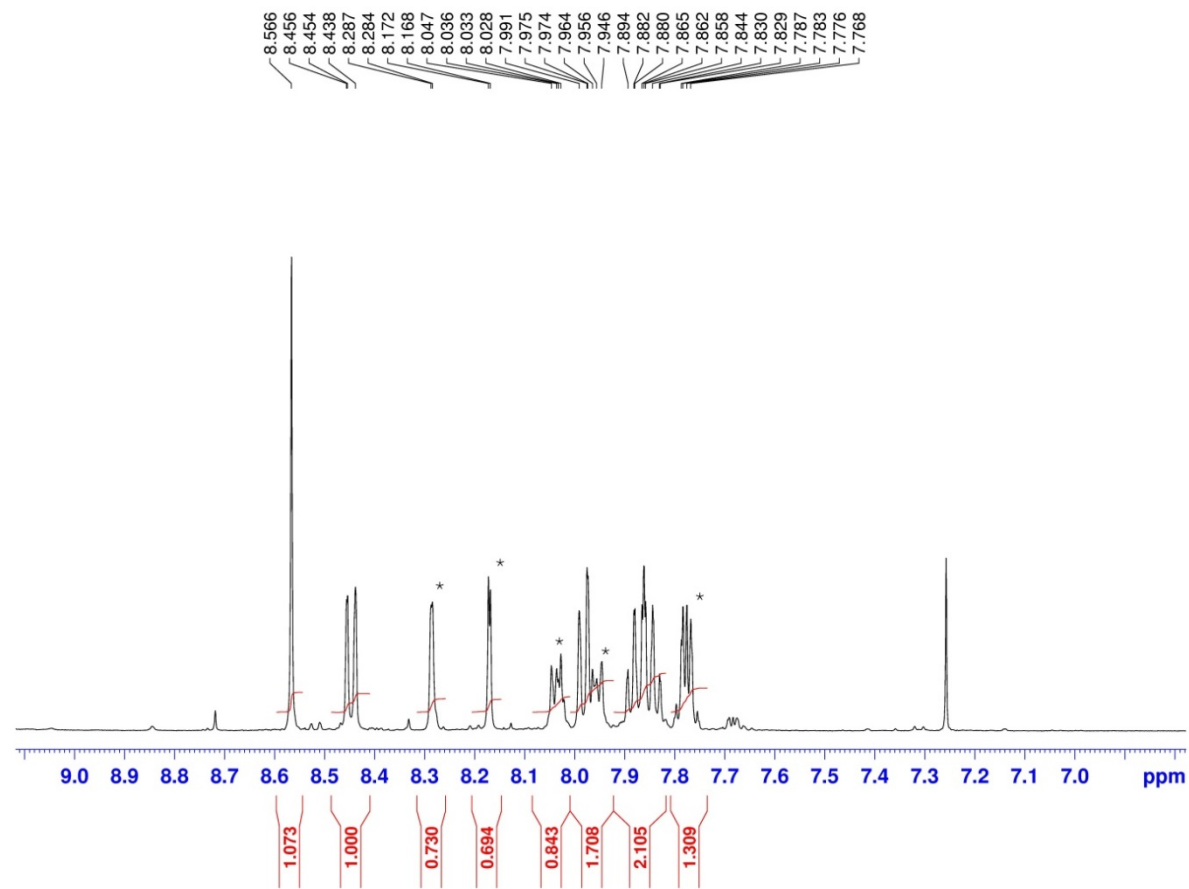
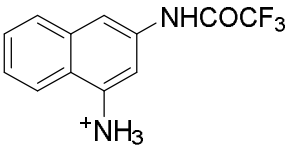


Figure 14. <sup>1</sup>H NMR spectrum of **29** in CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>D.

**29:** <sup>1</sup>H (500.13 MHz, CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H, 273 K) δ 7.75-7.81 (2 H, m, 6,7-H<sub>2</sub>), 7.95 (1 H, m, 8-H), 8.04 (1 H, m, 5-H), 8.18 (1 H, d, *J* 1.9 Hz, 2-H), 8.29 (1 H, s, 4-H), 9.31 (NH); <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H, 273 K) δ 116.10 (q, *J* 103.7 Hz, CF<sub>3</sub>), 116.48 (2-C), 119.63 (8-C), 123.08 (4-C), 125.15 (8a-C), 125.91 (1-C), 129.74 (6-C), 129.79 (5-C), 129.80 (7-C), 131.52 (3-C), 134.81 (4a-C), 157.58 (q, *J* 39.1 Hz, C=O).



**Figure 15.** <sup>1</sup>H NMR spectrum of **29** and **30** (\*) 48 h after dissolution of **26** in CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>D.

Spectra of synthesised compounds

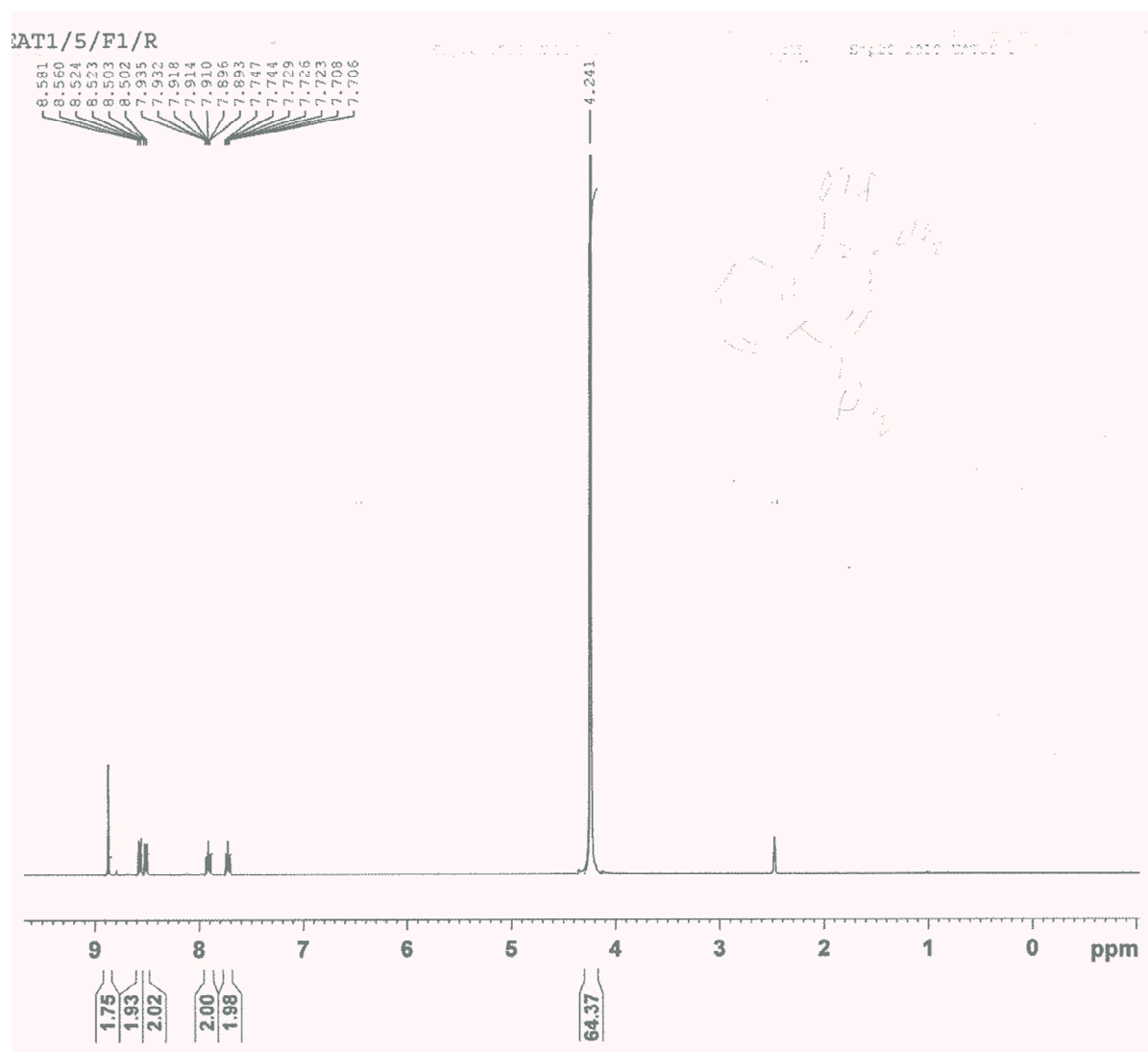
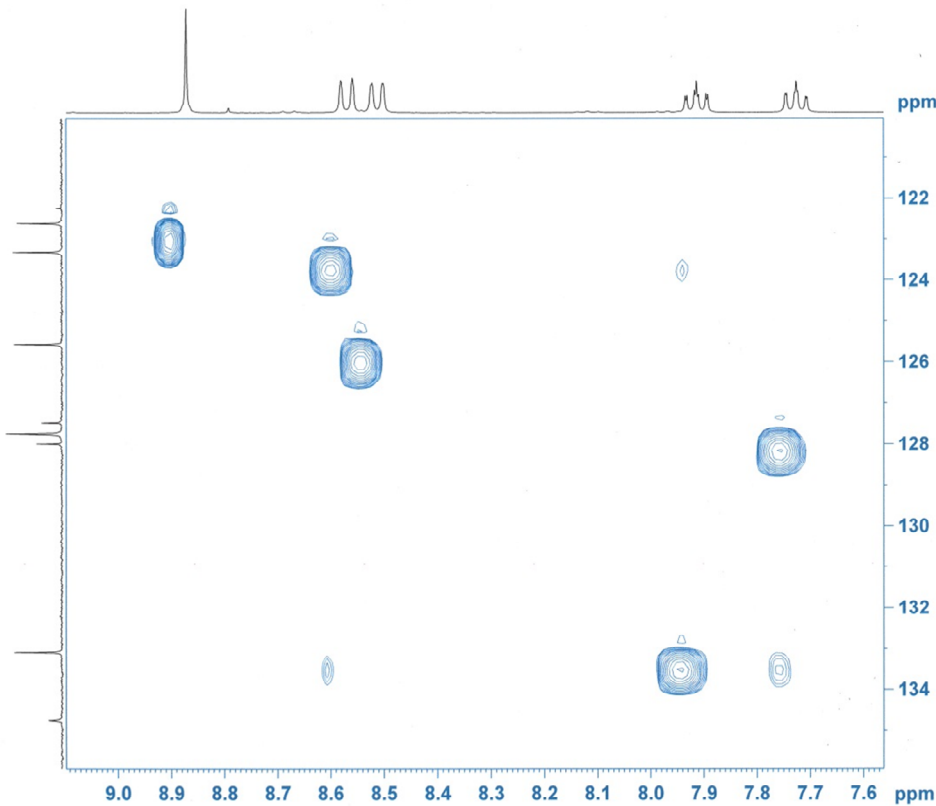


Figure 16.  $^1\text{H}$  NMR spectrum of **7** in  $(\text{CD}_3)_2\text{SO}$ .

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**Figure 18.** HSQC NMR spectrum of **7** in (CD<sub>3</sub>)<sub>2</sub>SO.

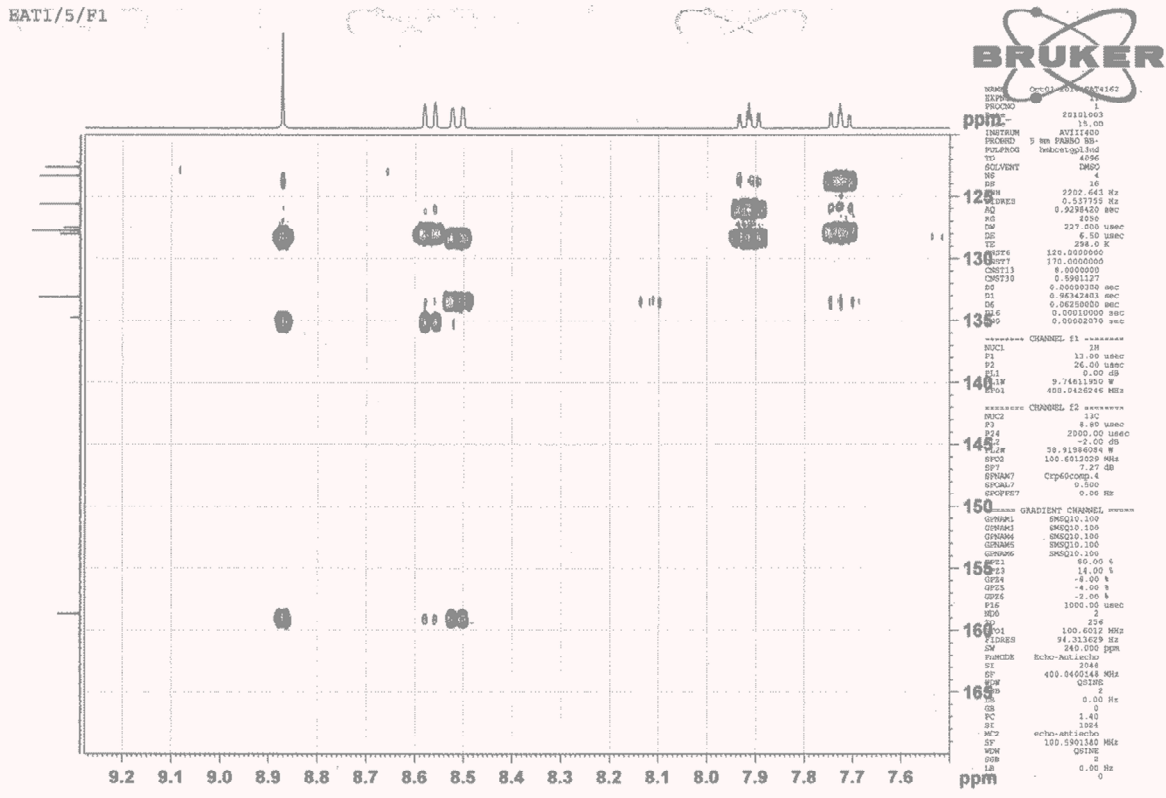


Figure 19. HMBC NMR spectrum of 7 in  $(\text{CD}_3)_2\text{SO}$ .

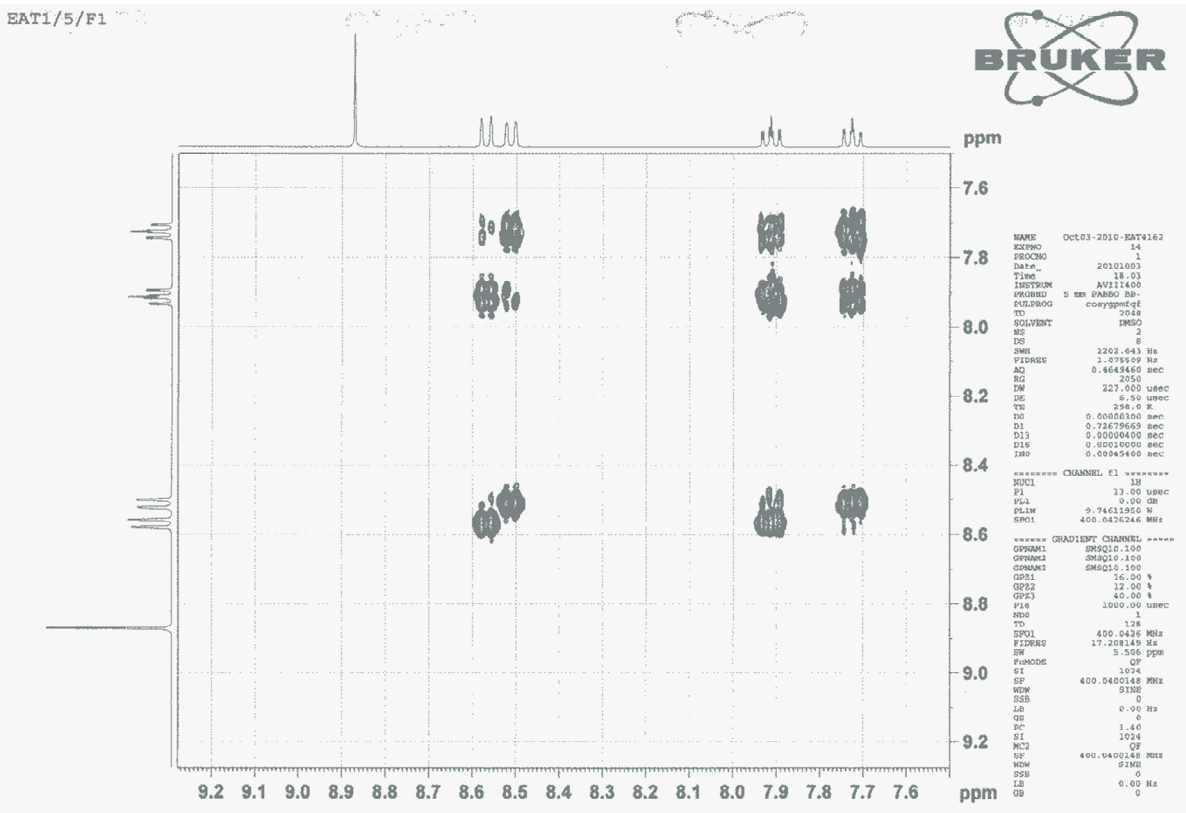


Figure 20.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of 7 in  $(\text{CD}_3)_2\text{SO}$ .

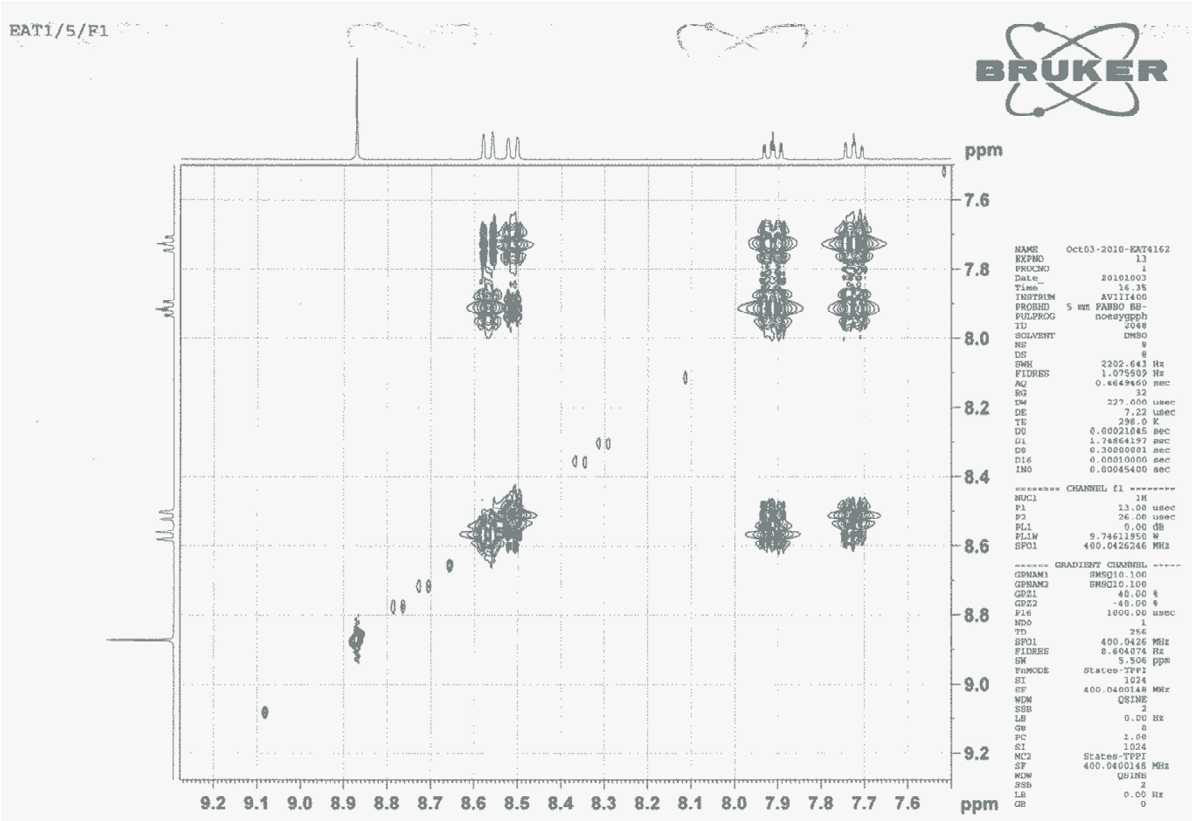


Figure 21.  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of **7** in  $(\text{CD}_3)_2\text{SO}$ .

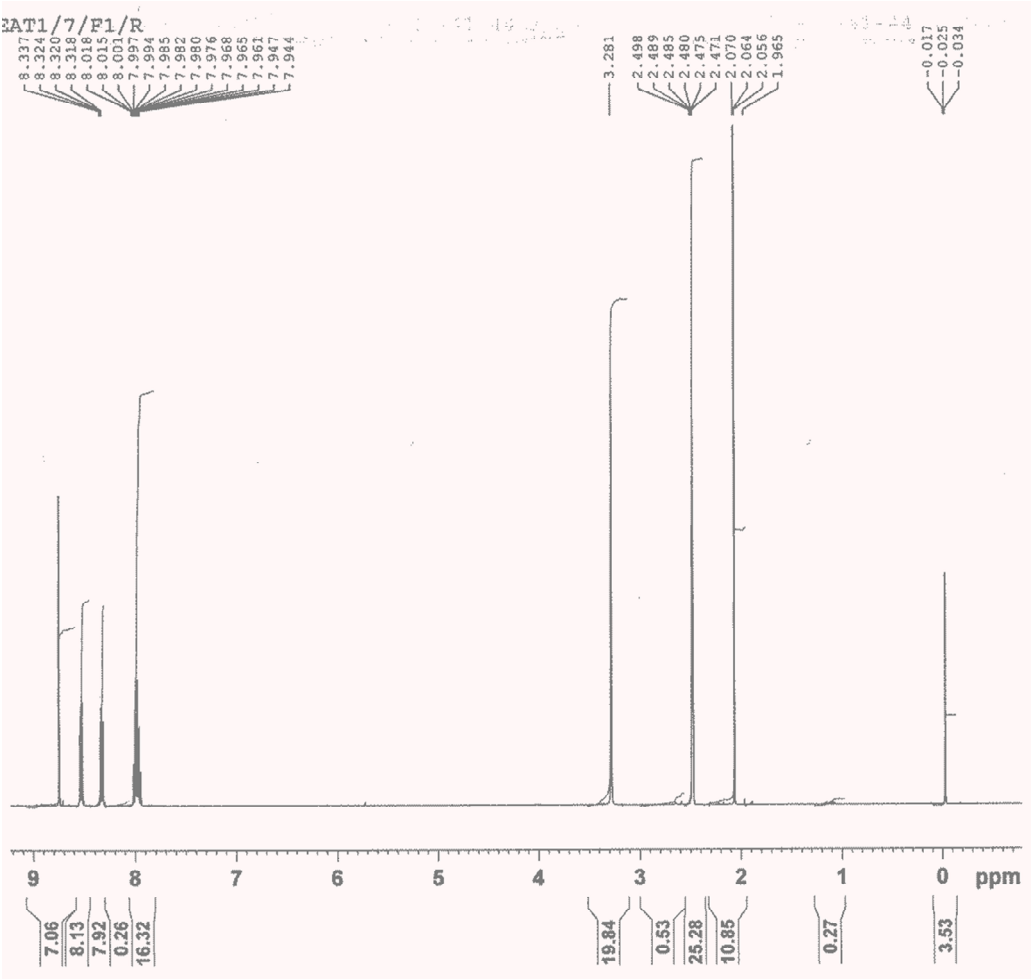
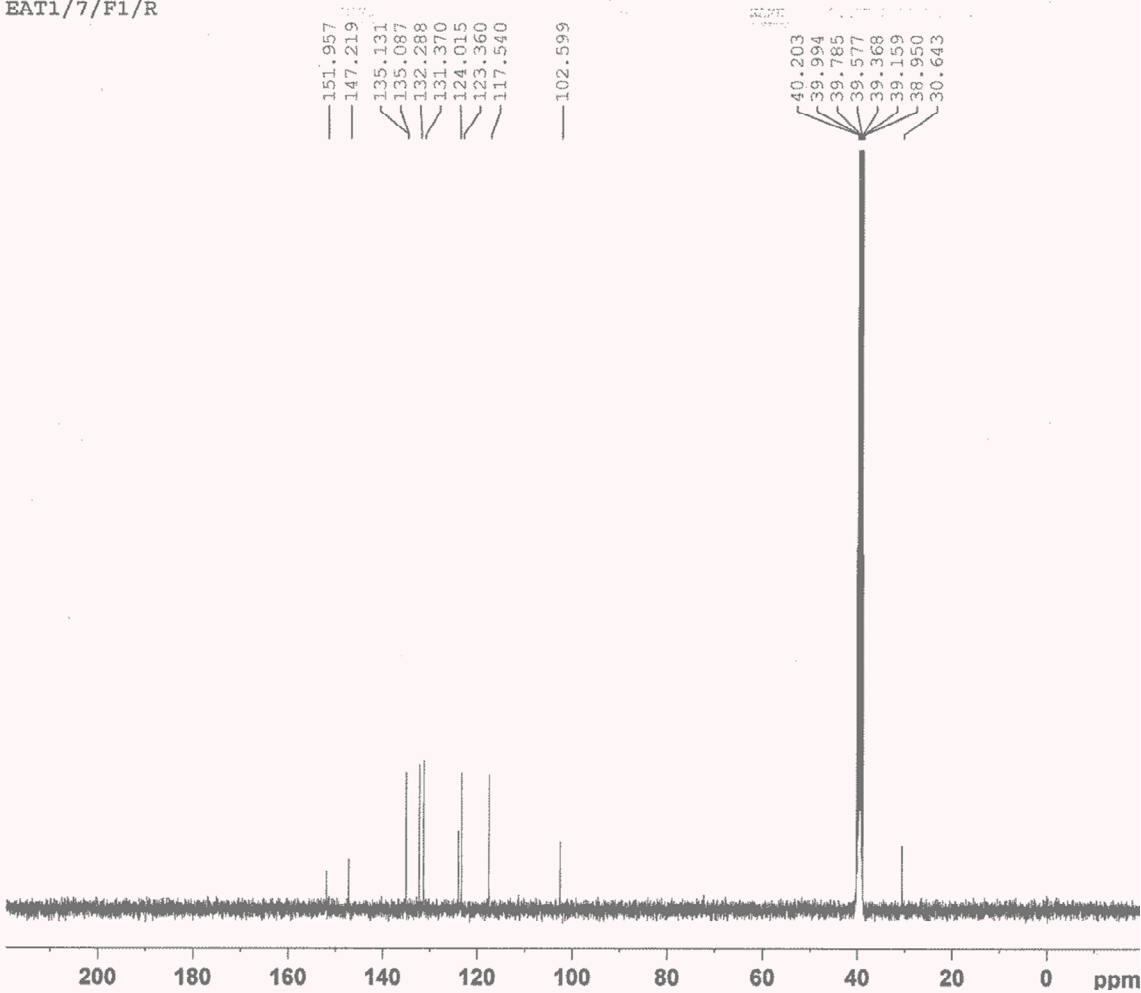


Figure 22.  $^1\text{H}$  NMR spectrum of **8** in  $(\text{CD}_3)_2\text{SO}$ .

[illegible]

**Figure 24.** HSQC NMR spectrum of **8** in (CD<sub>3</sub>)<sub>2</sub>SO.

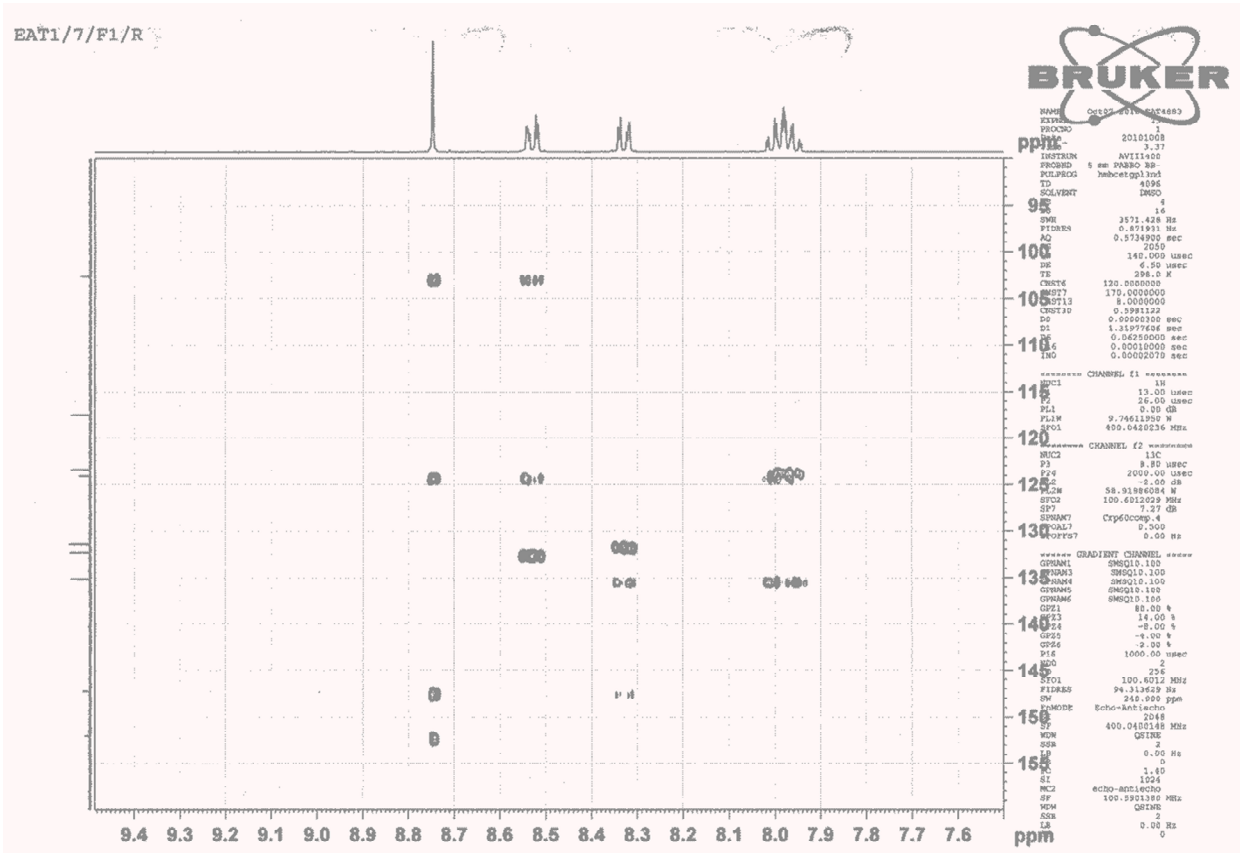


Figure 25. HMBC NMR spectrum of **8** in  $(\text{CD}_3)_2\text{SO}$ .

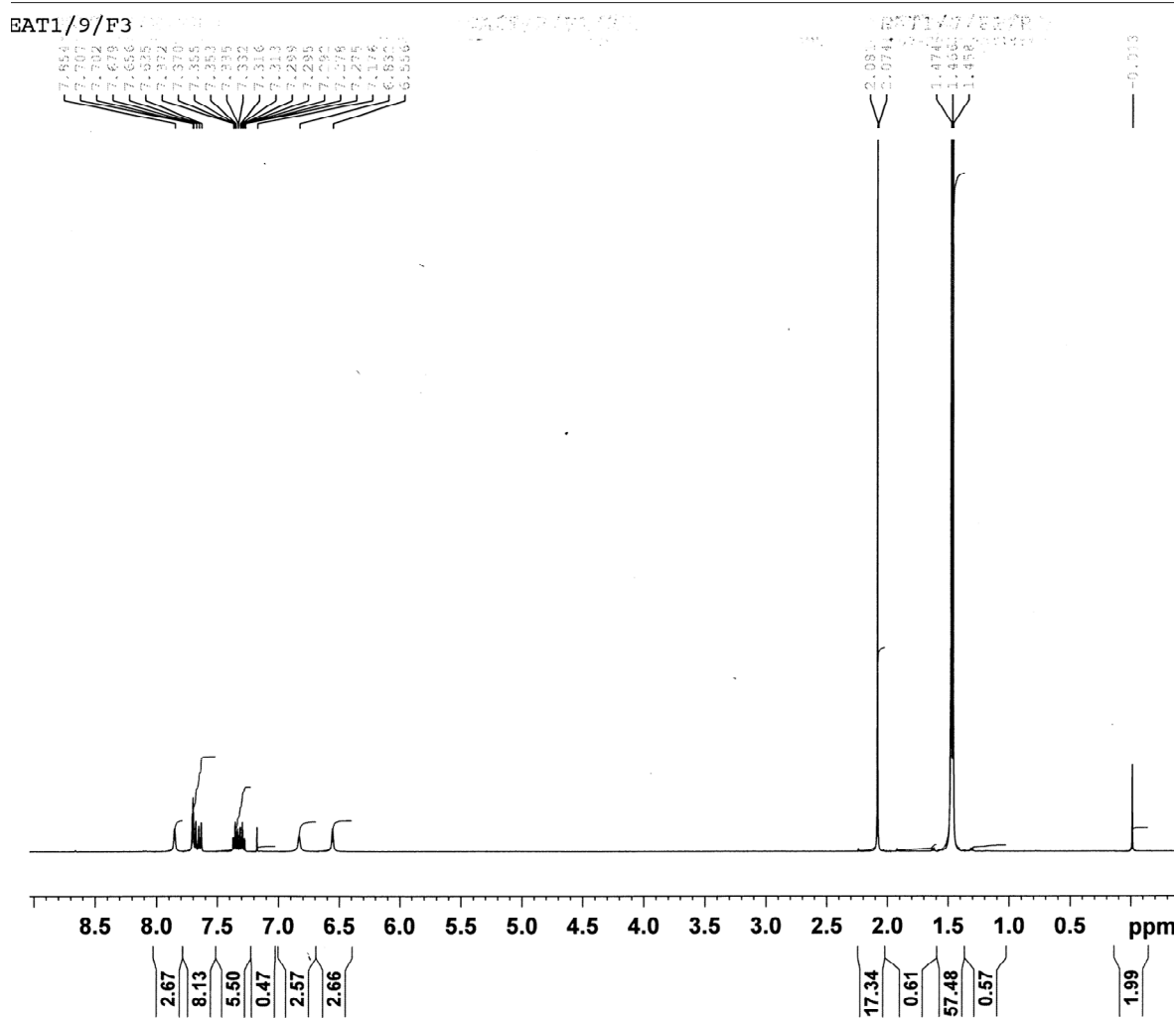


Figure 26.  $^1\text{H}$  NMR spectrum of **10** in  $\text{CDCl}_3$ .



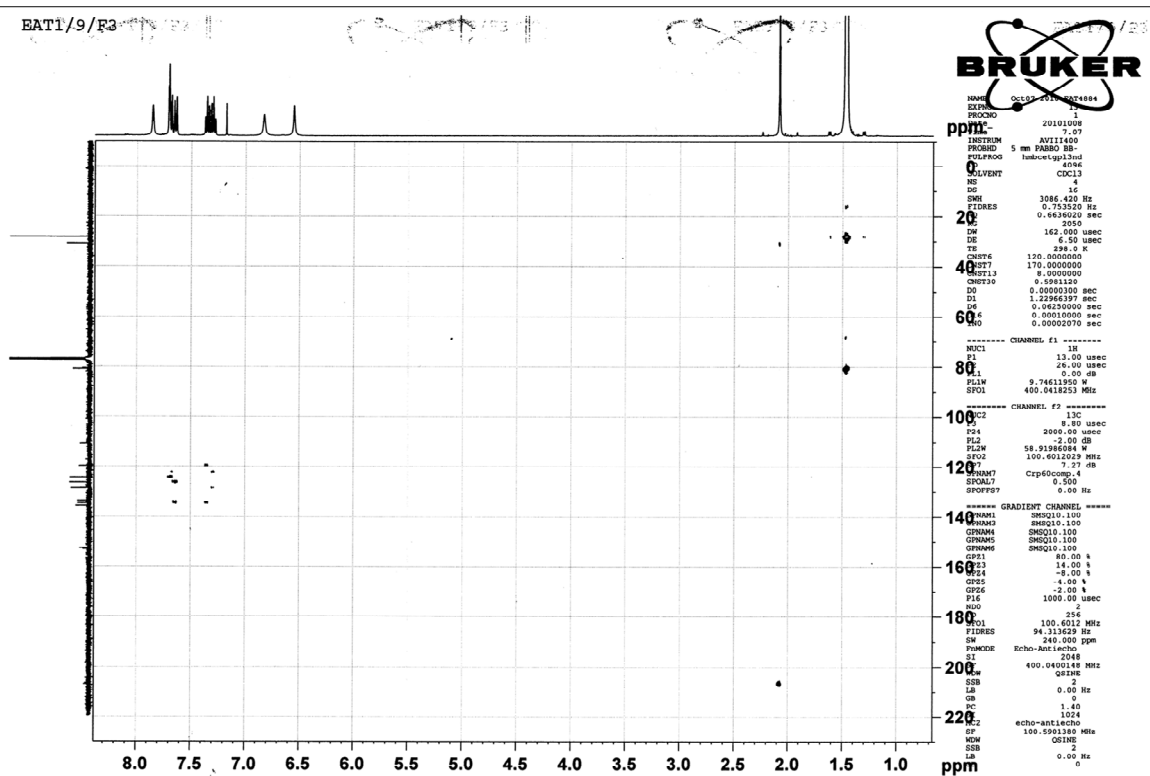


Figure 29. HMBC NMR spectrum of **10** in  $\text{CDCl}_3$ .

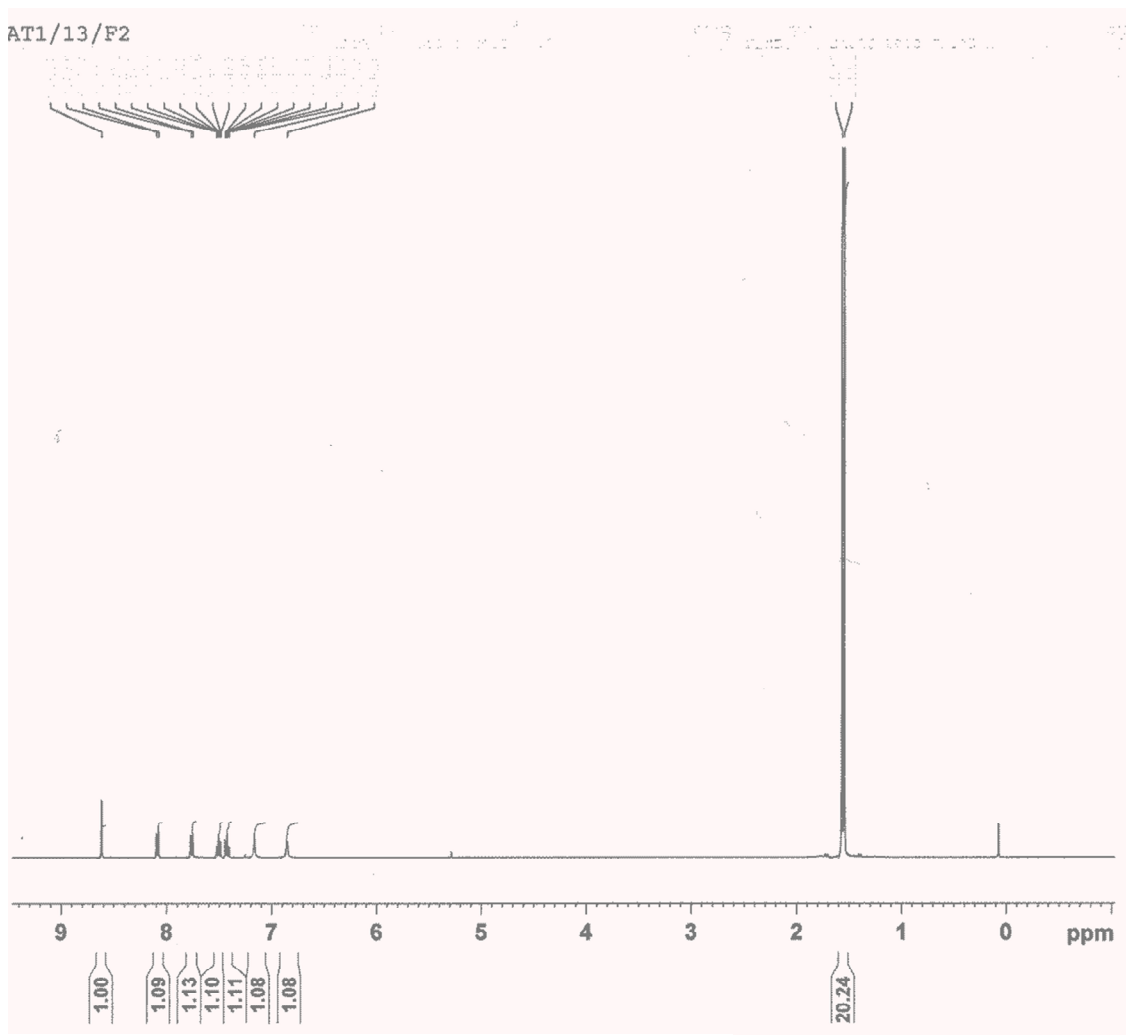


Figure 30.  $^1\text{H}$  NMR spectrum of **11** in  $\text{CDCl}_3$ .

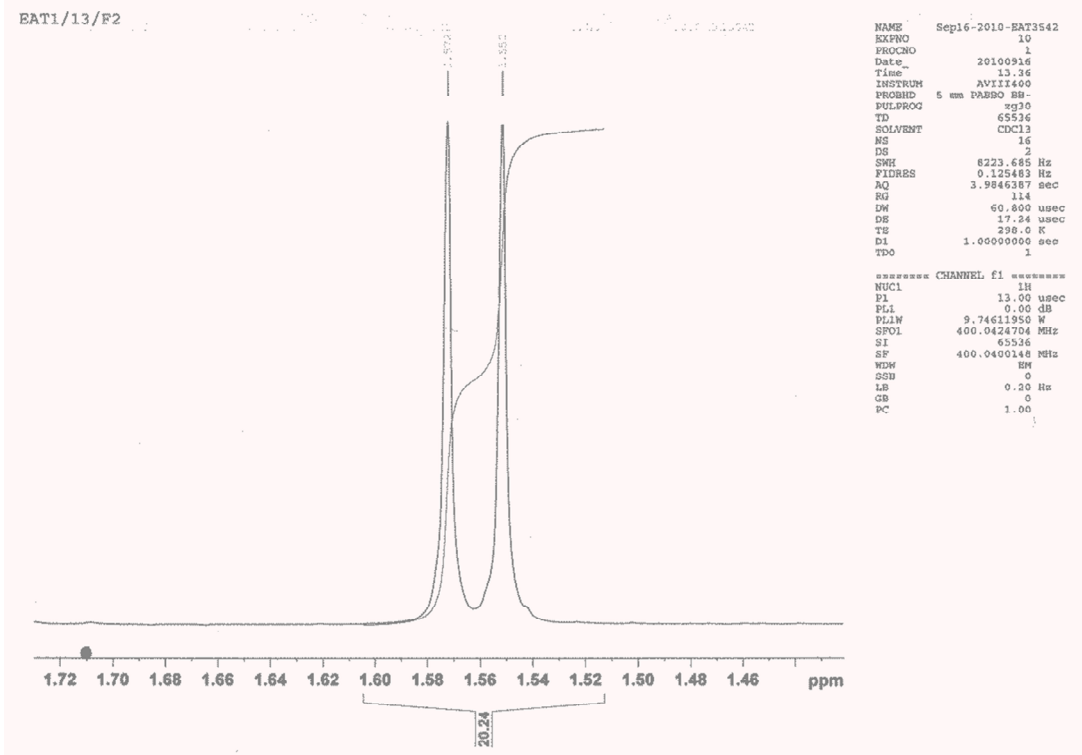


Figure 31. Expansion of part of  $^1\text{H}$  NMR spectrum of **11** in  $\text{CDCl}_3$ .

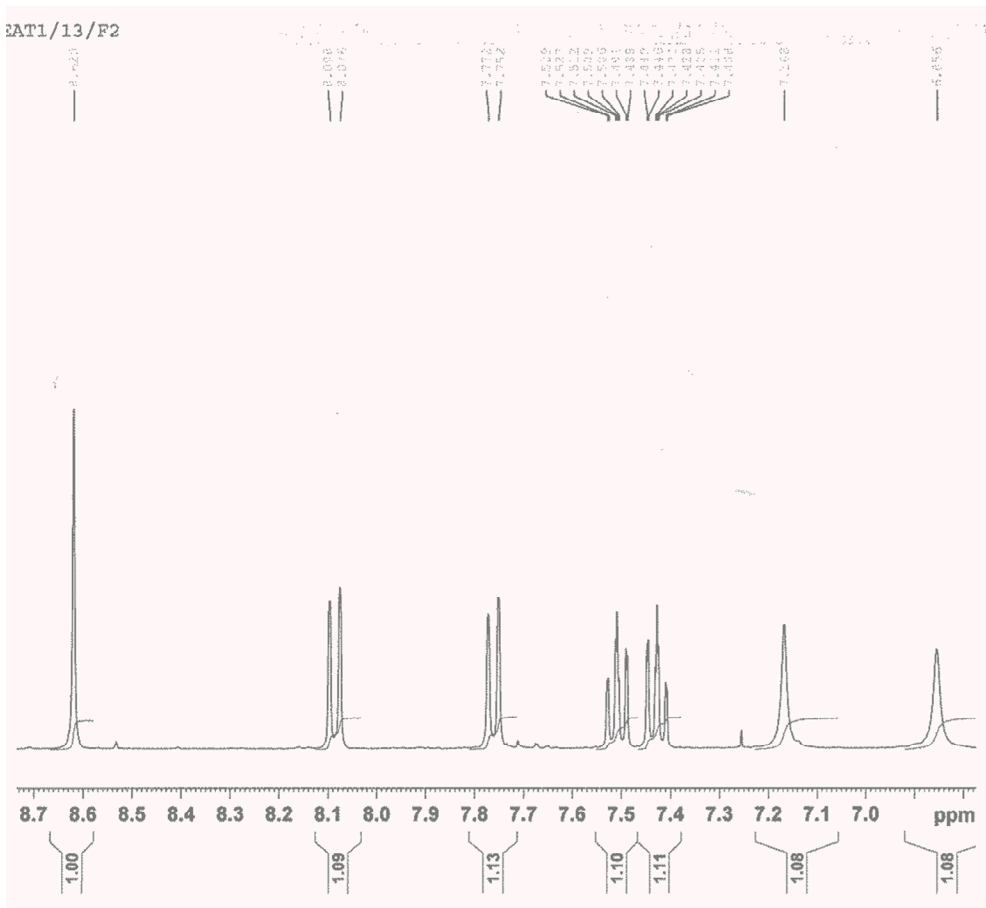


Figure 32. Expansion of part of  $^1\text{H}$  NMR spectrum of **11** in  $\text{CDCl}_3$ .

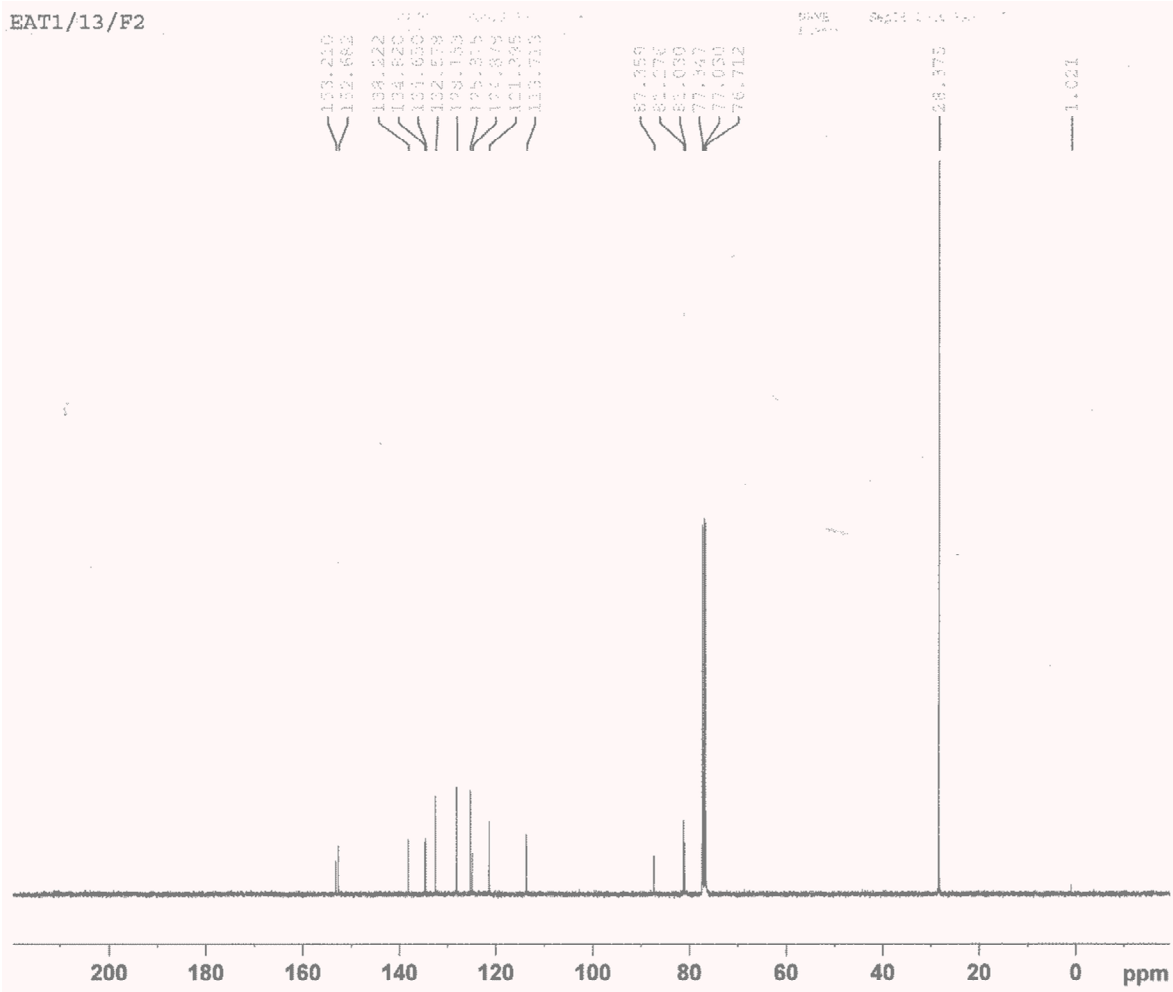


Figure 33. <sup>13</sup>C NMR spectrum of **11** in CDCl<sub>3</sub>.

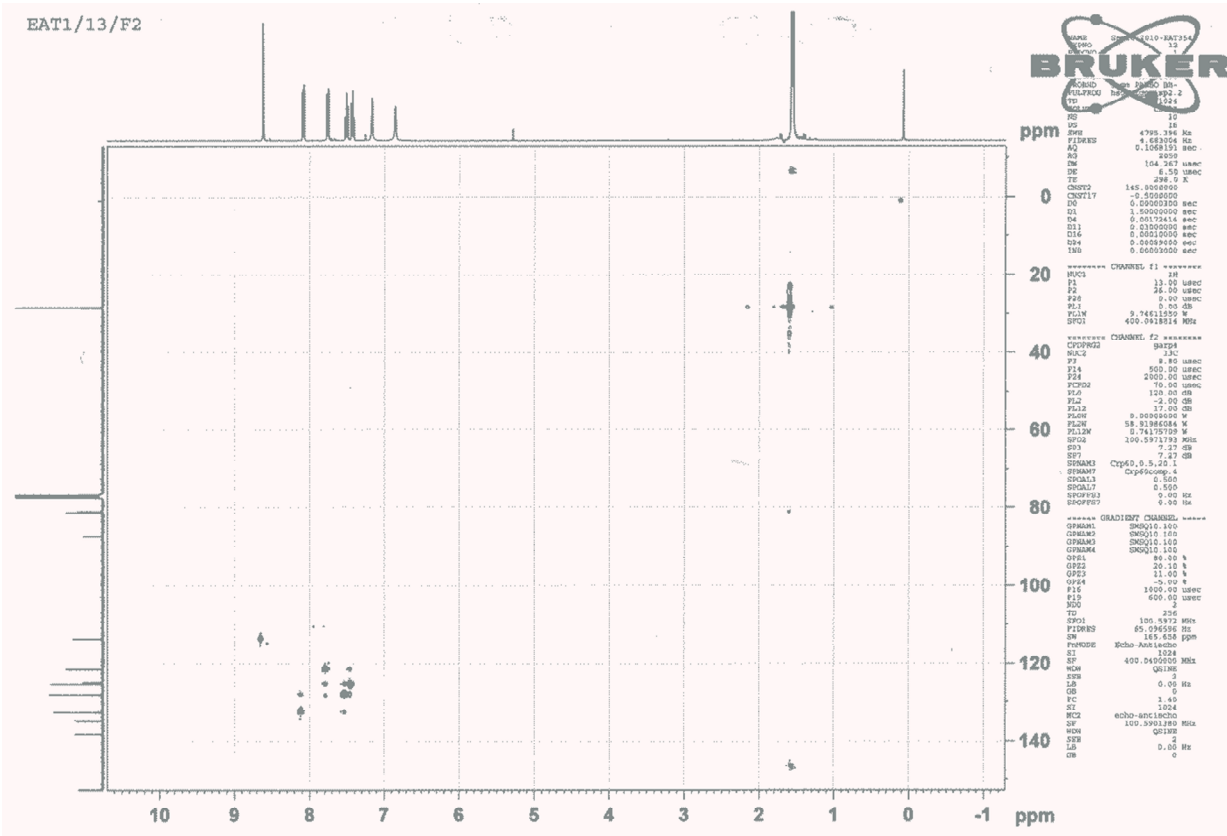


Figure 34. HSQC NMR spectrum of **11** in CDCl<sub>3</sub>.

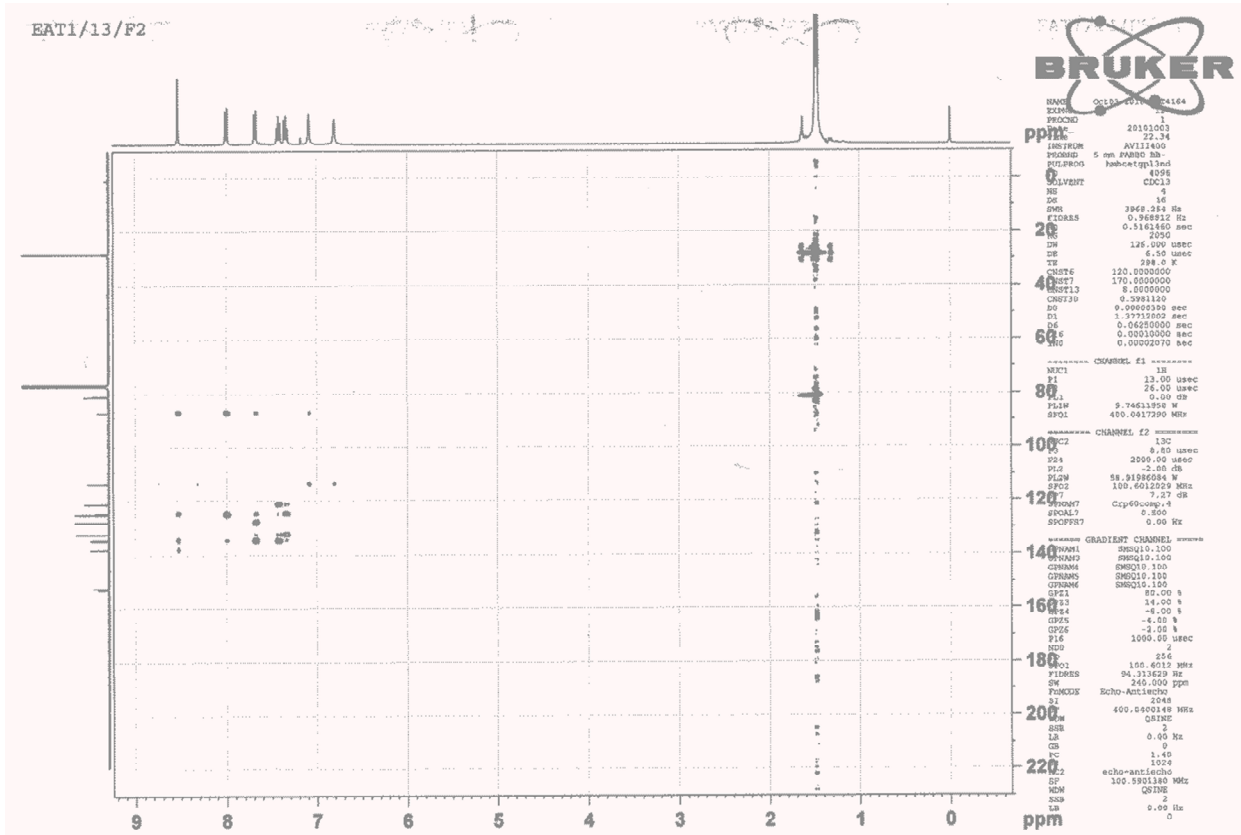


Figure 35. HMBC NMR spectrum of **11** in CDCl<sub>3</sub>.

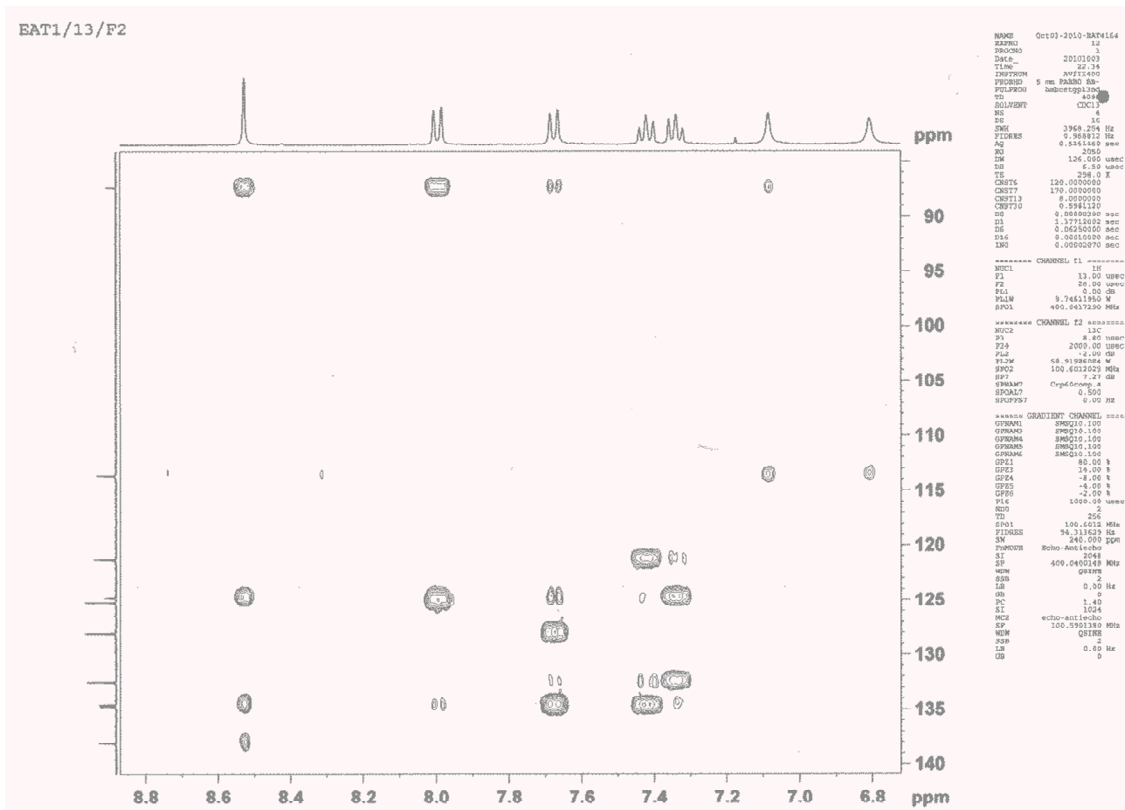


Figure 36. Expansion of part of HMBC NMR spectrum of **11** in CDCl<sub>3</sub>.

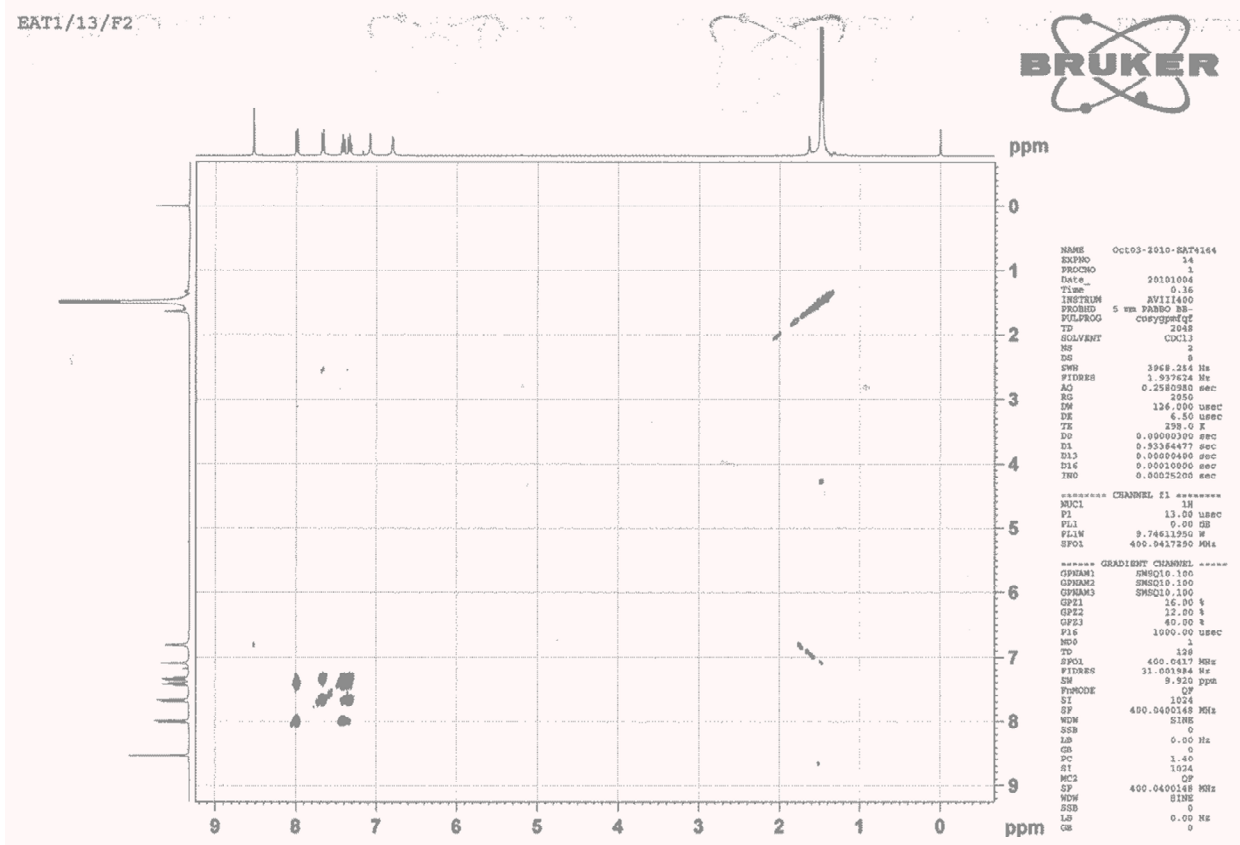


Figure 37.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **11** in  $\text{CDCl}_3$ .

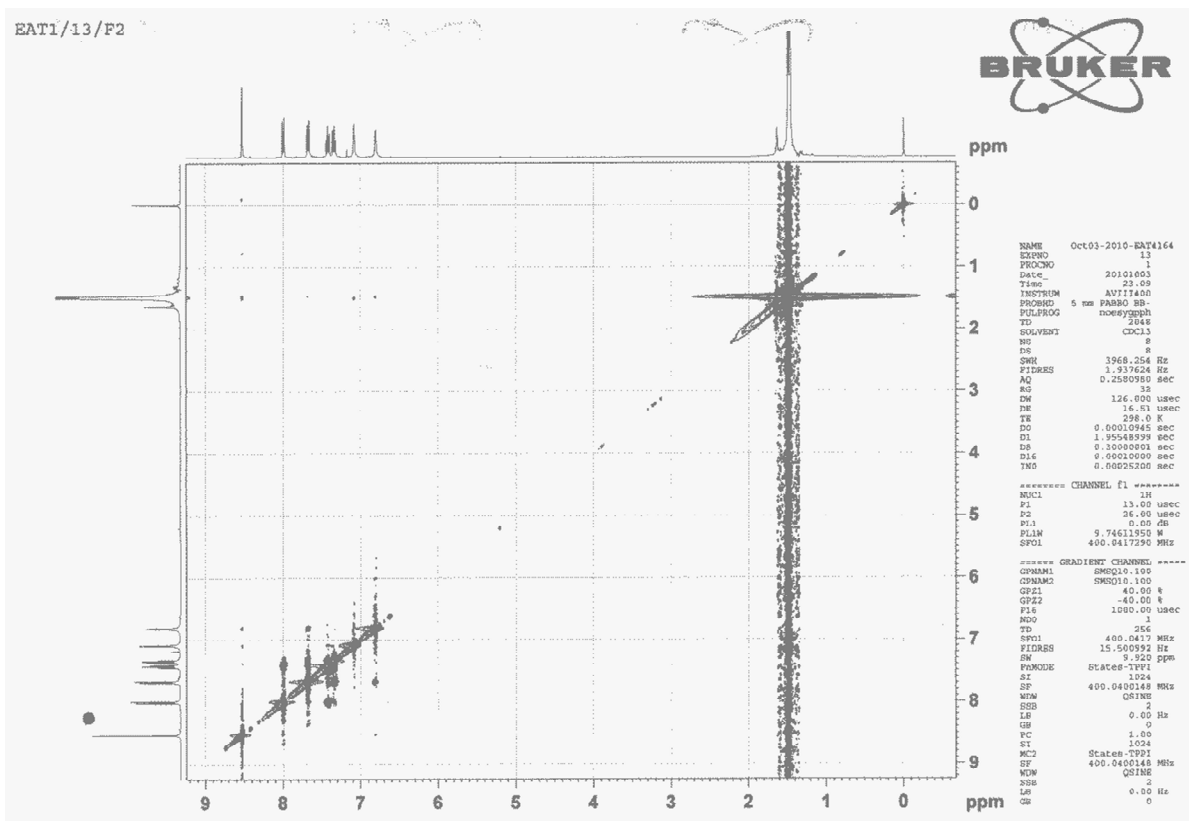


Figure 38.  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of **11** in  $\text{CDCl}_3$ .

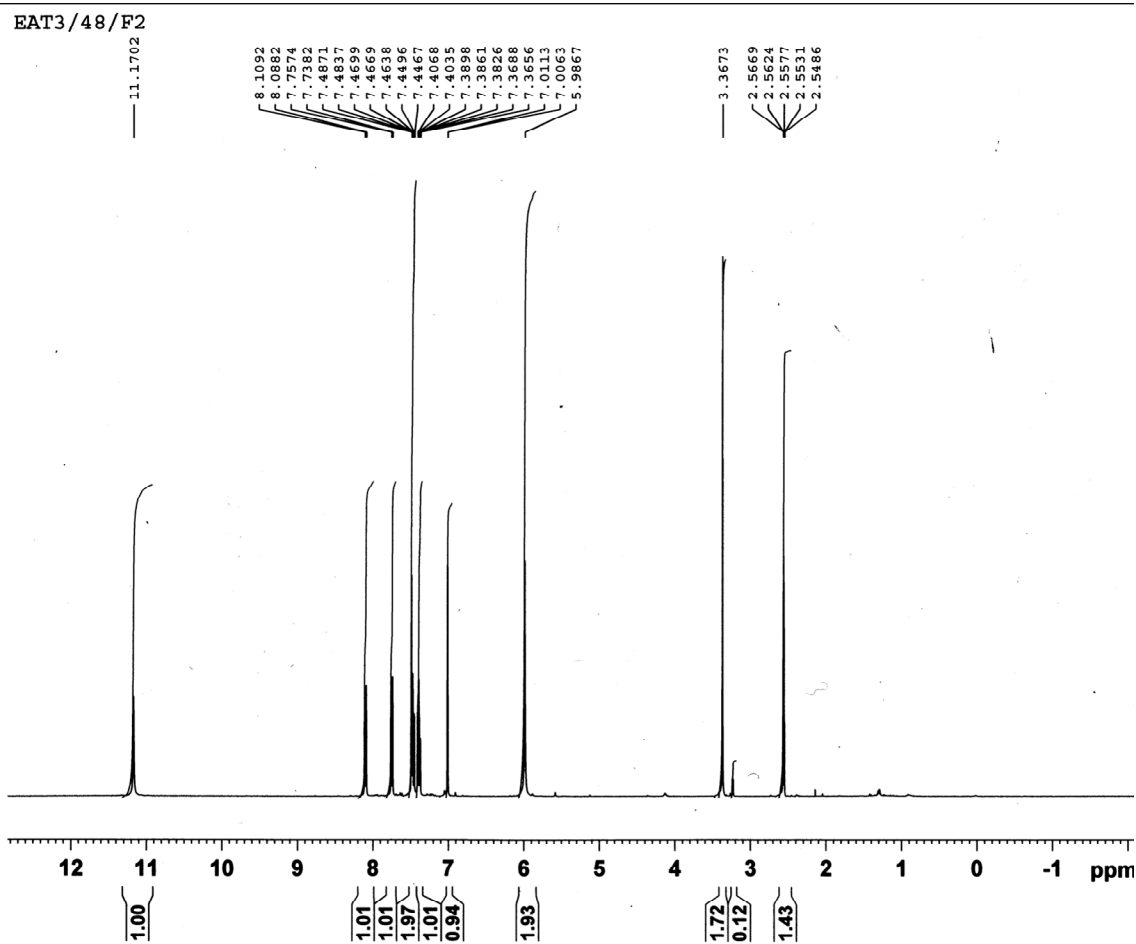


Figure 39.  $^1\text{H}$  NMR spectrum of **24** in  $(\text{CD}_3)_2\text{SO}$ .

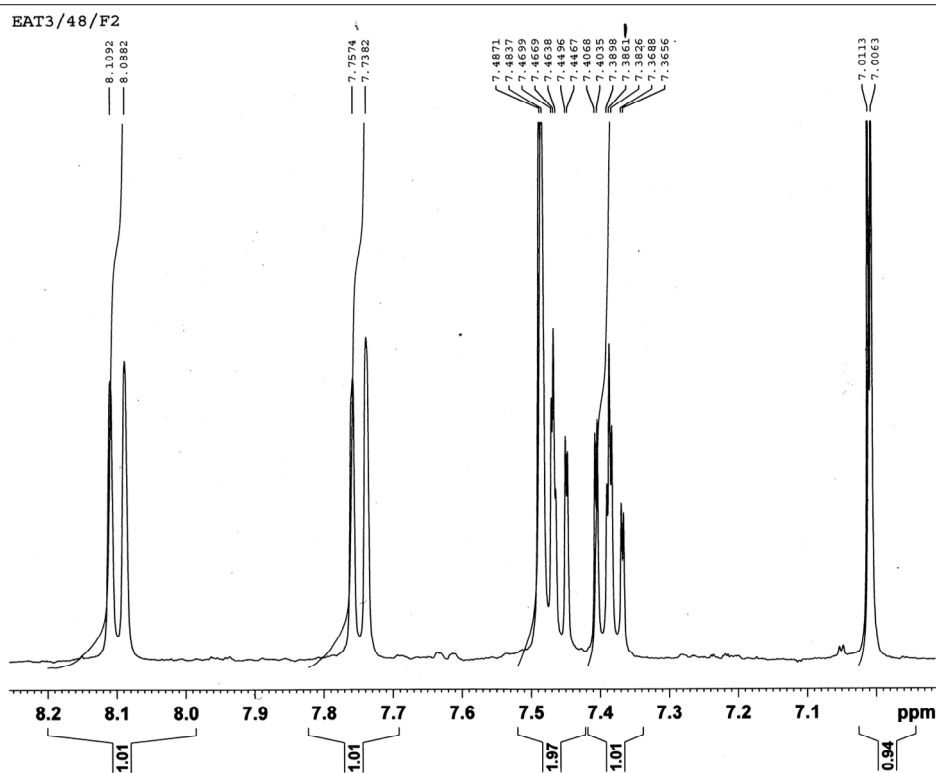


Figure 40. Expansion of part of  $^1\text{H}$  NMR spectrum of **24** in  $(\text{CD}_3)_2\text{SO}$ .

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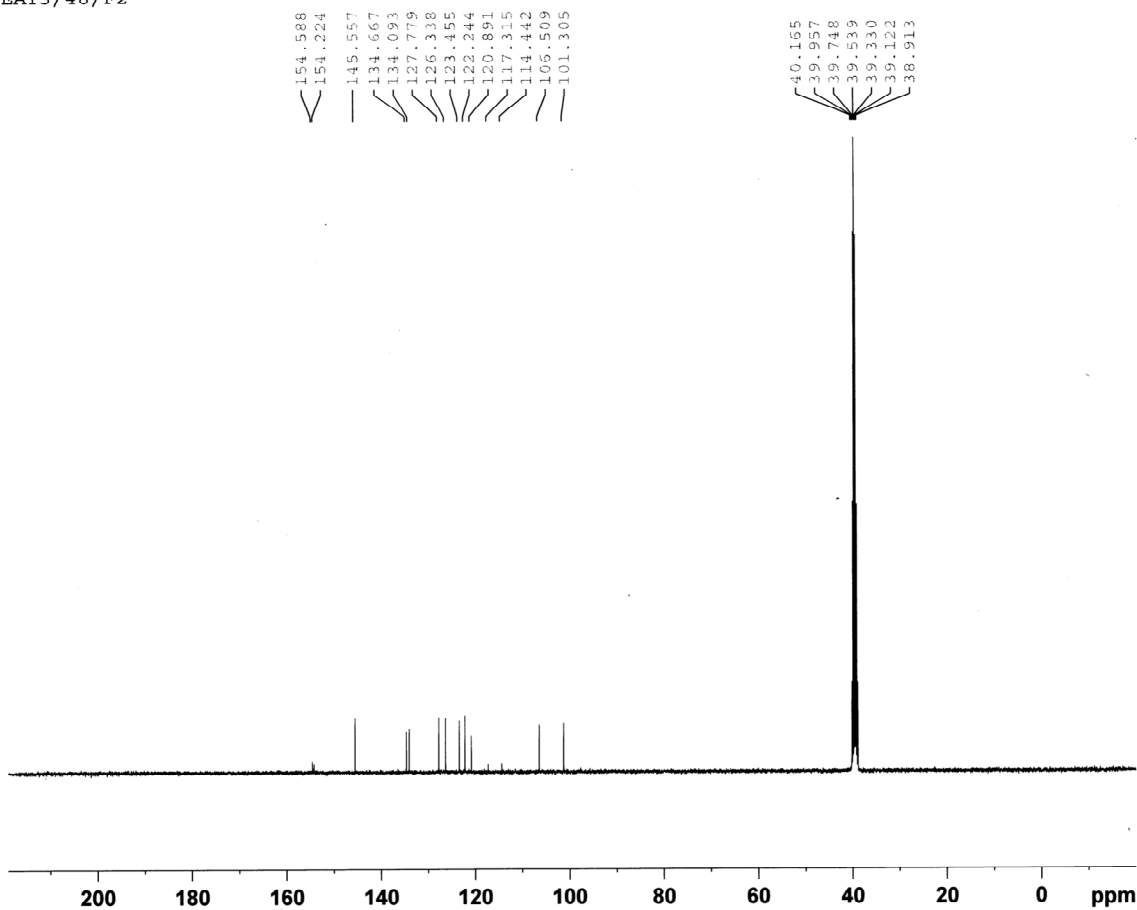


Figure 41. <sup>13</sup>C NMR spectrum of **24** in (CD<sub>3</sub>)<sub>2</sub>SO.

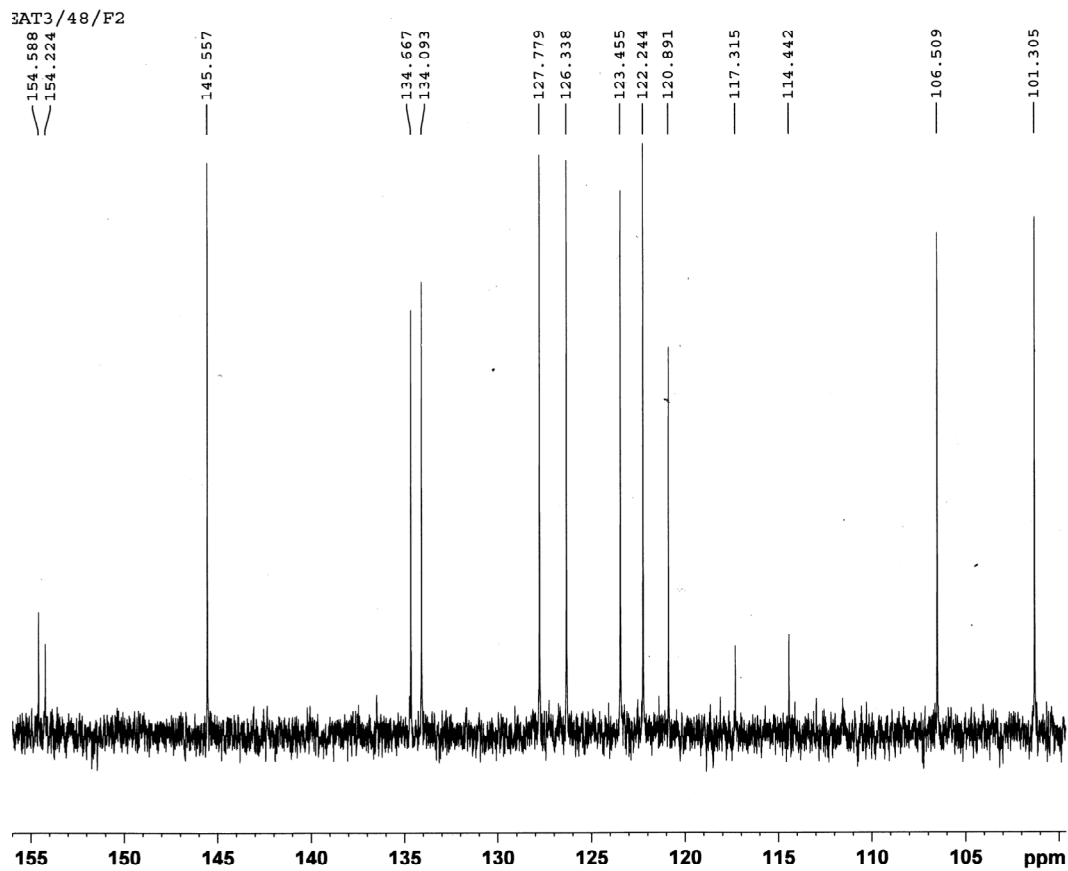
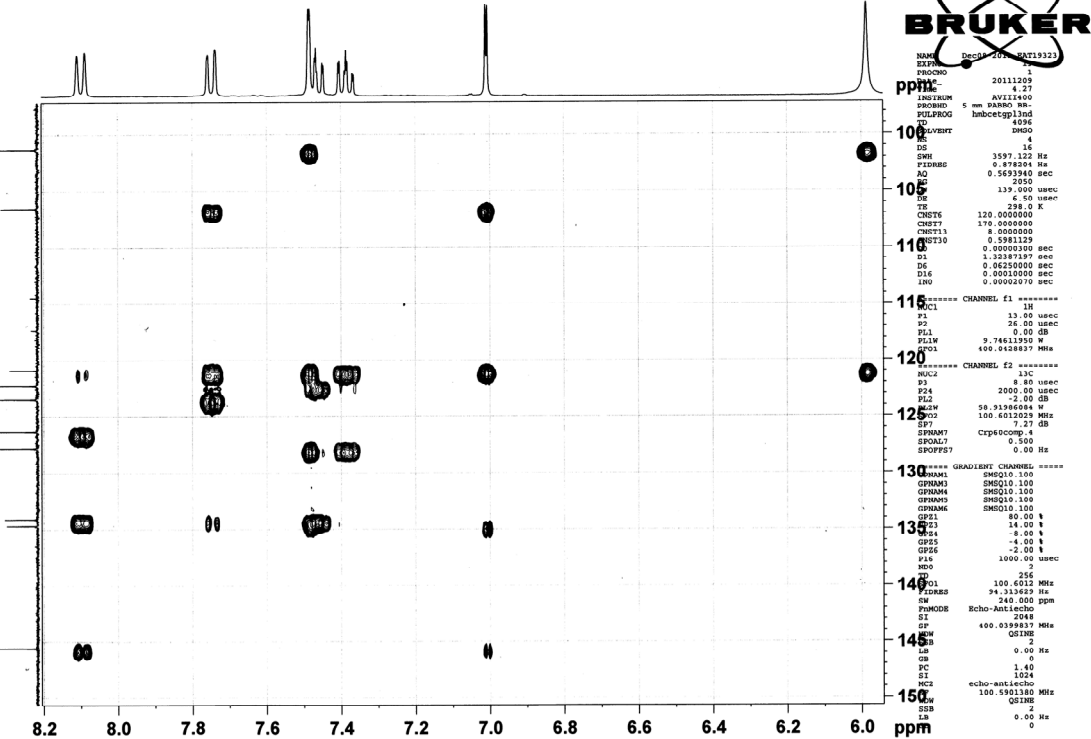


Figure 42. Expansion of part of <sup>13</sup>C NMR spectrum of **24** in (CD<sub>3</sub>)<sub>2</sub>SO.



**Figure 44.** HMBC NMR spectrum of **24** in (CD<sub>3</sub>)<sub>2</sub>SO.

EAT3/48/F2

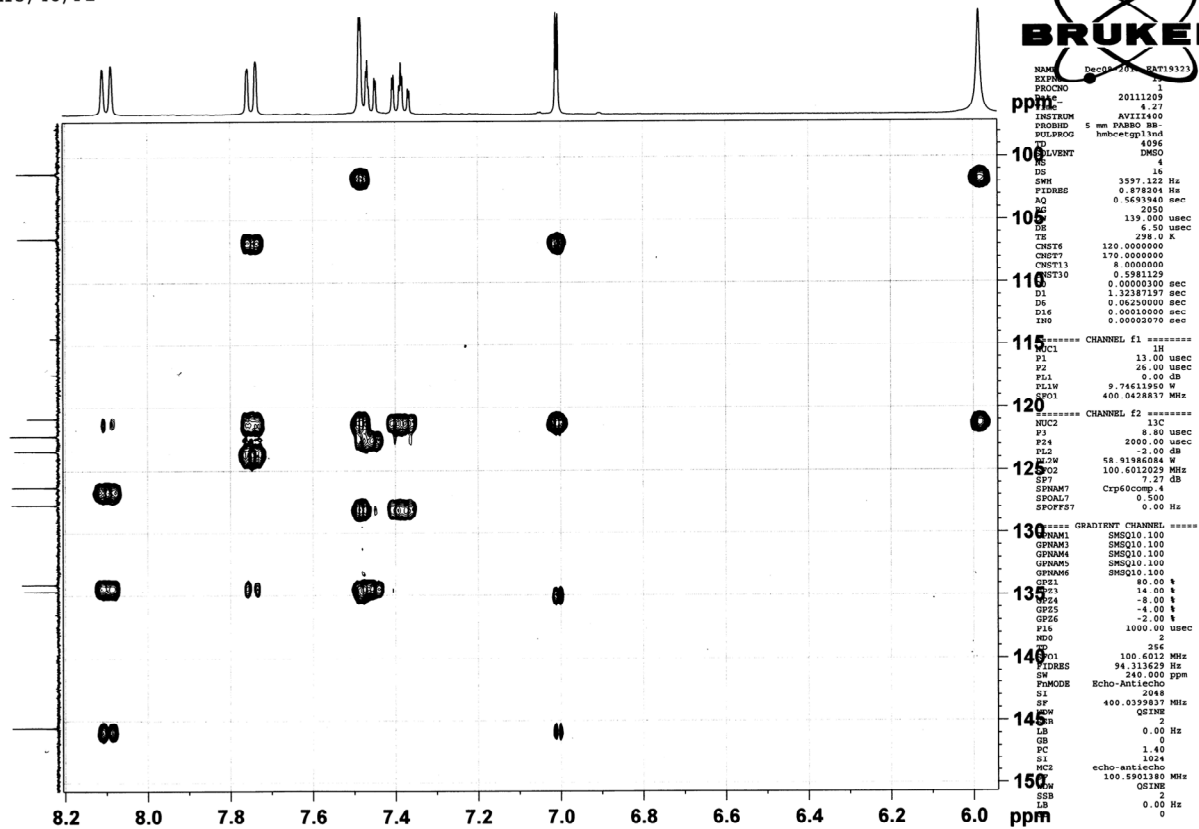


Figure 45. Expansion of part of HMBC NMR spectrum of **24** in  $(\text{CD}_3)_2\text{SO}$ .

EAT3/48/F2

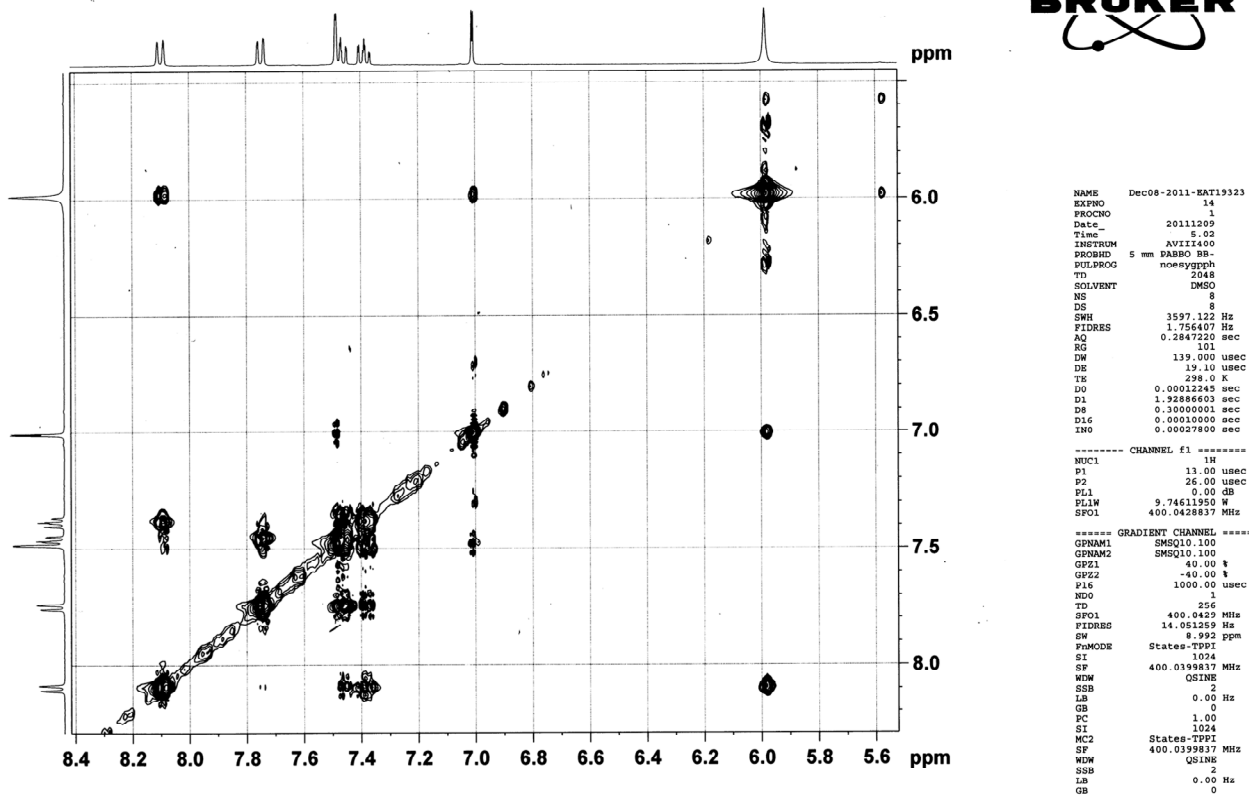


Figure 46.  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of **24** in  $(\text{CD}_3)_2\text{SO}$ .

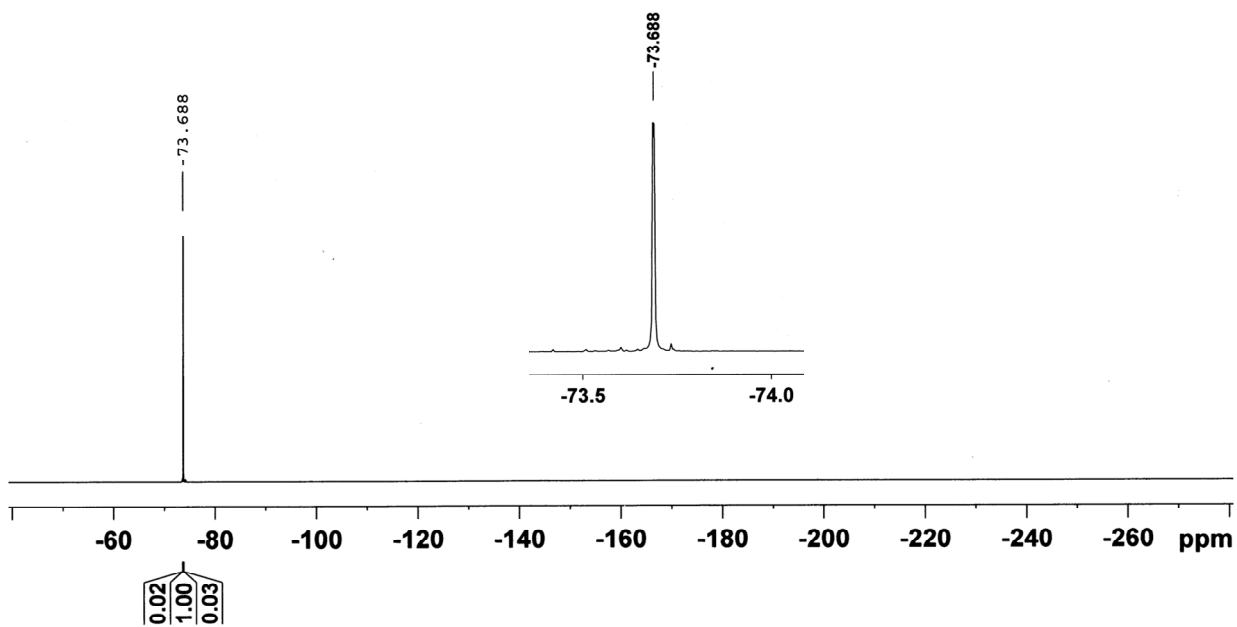


Figure 47.  $^{19}\text{F}$  NMR spectrum of **24** in  $(\text{CD}_3)_2\text{SO}$ .

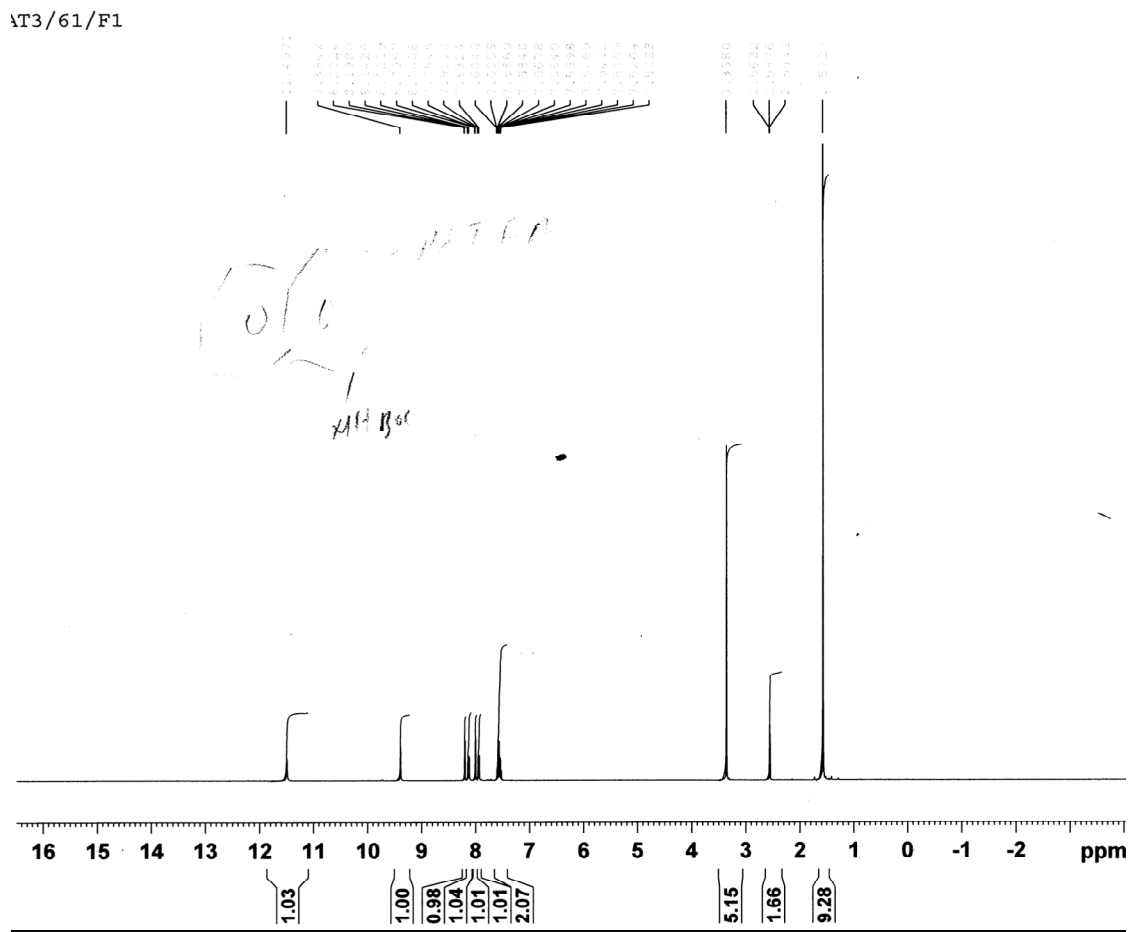


Figure 48.  $^1\text{H}$  NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .

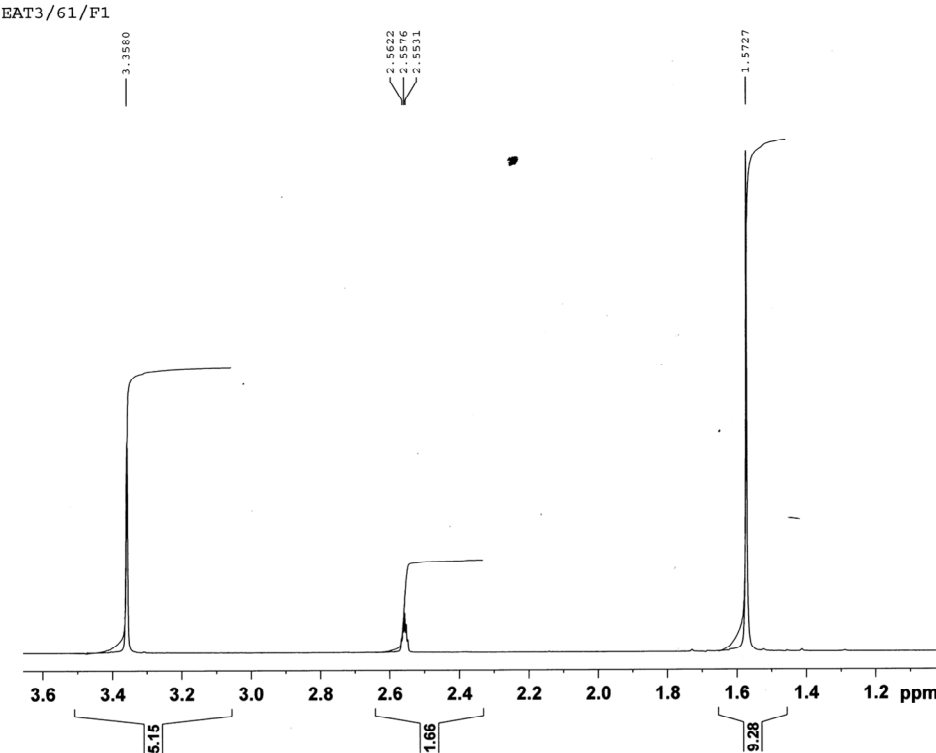


Figure 49. Expansion of part of  $^1\text{H}$  NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .

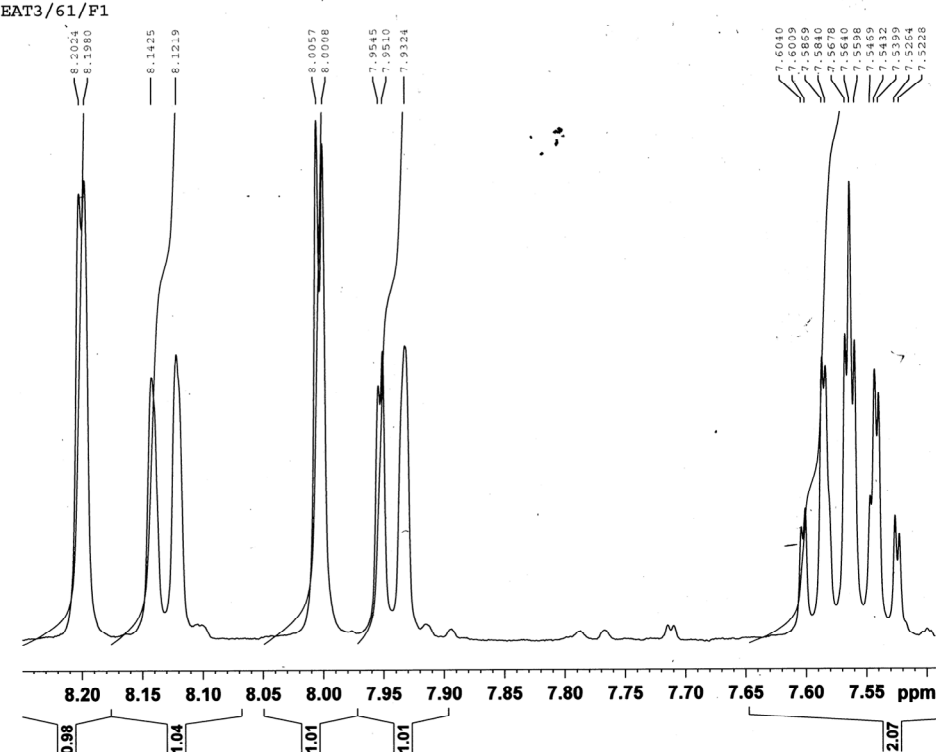


Figure 50. Expansion of part of  $^1\text{H}$  NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .

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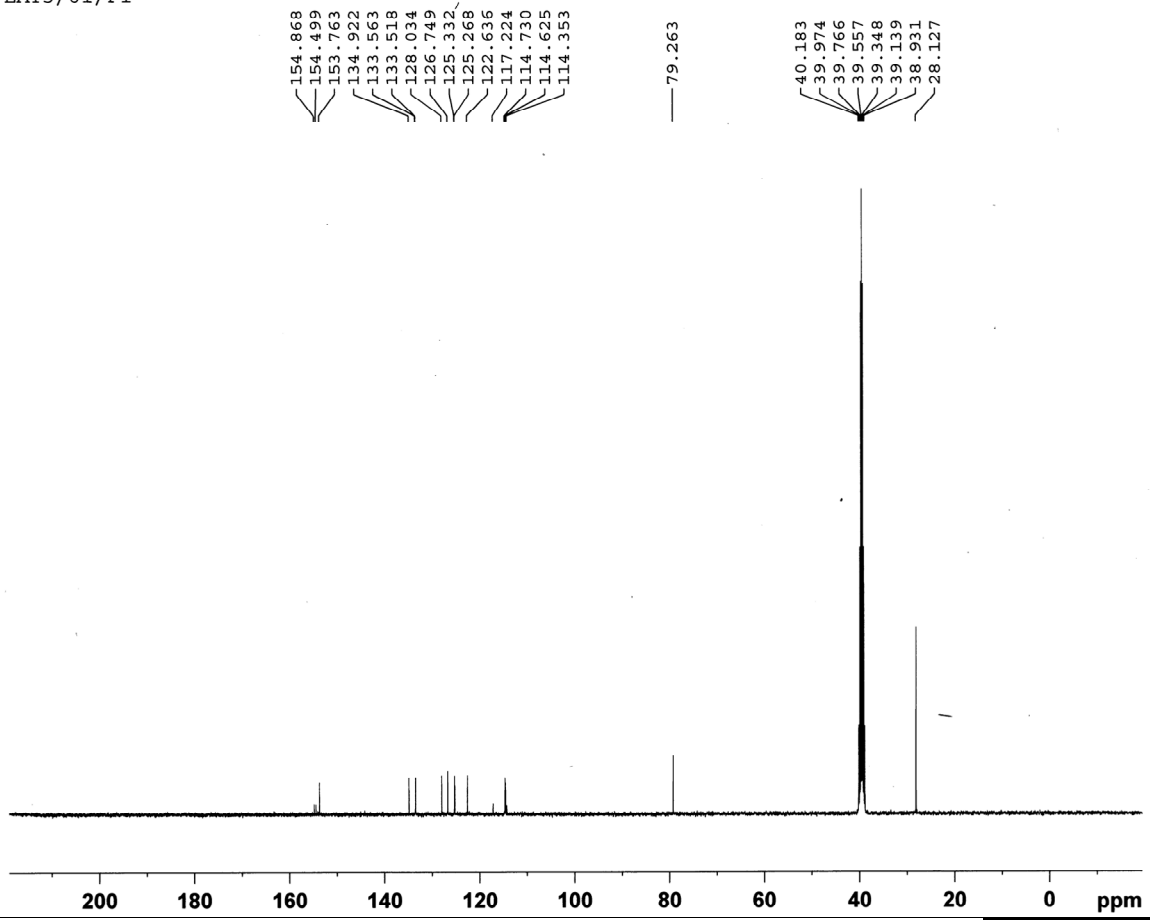


Figure 51.  $^{13}\text{C}$  NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .

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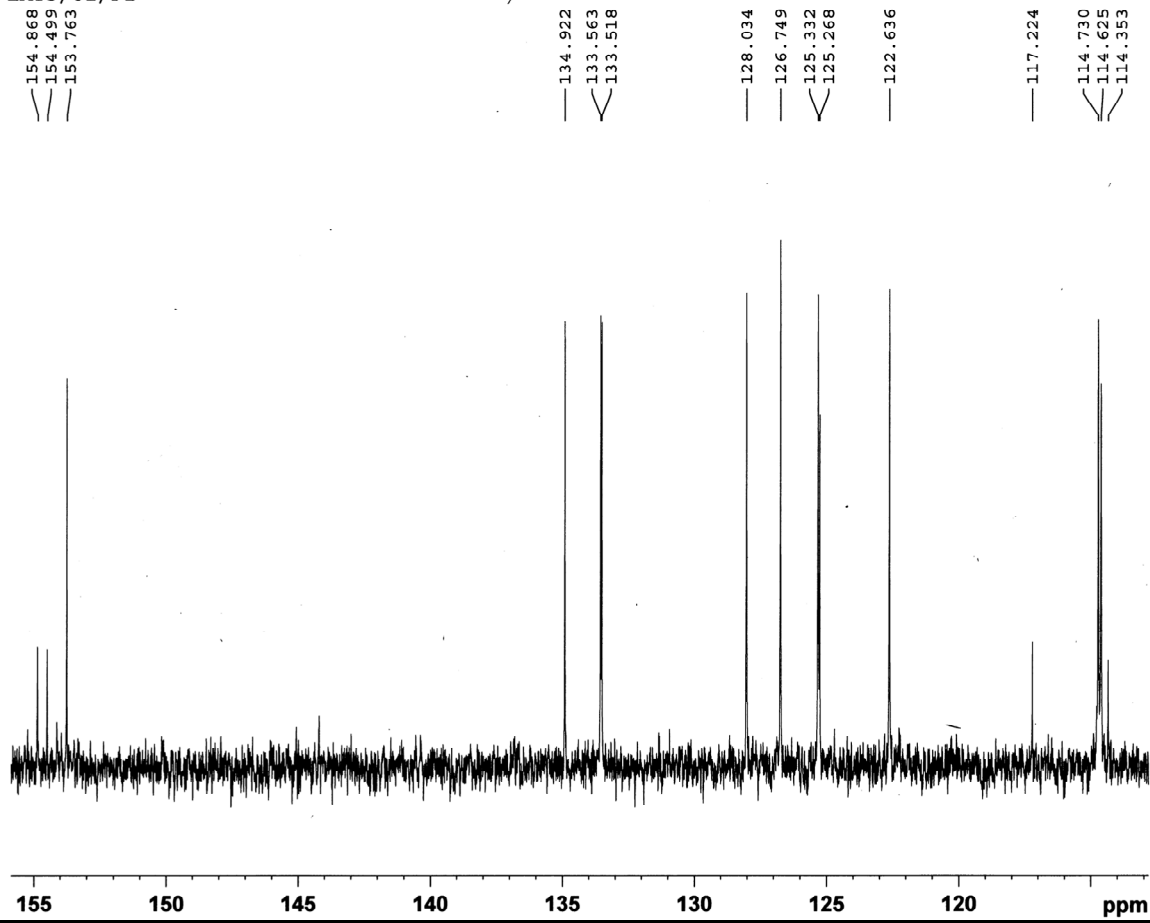
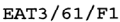
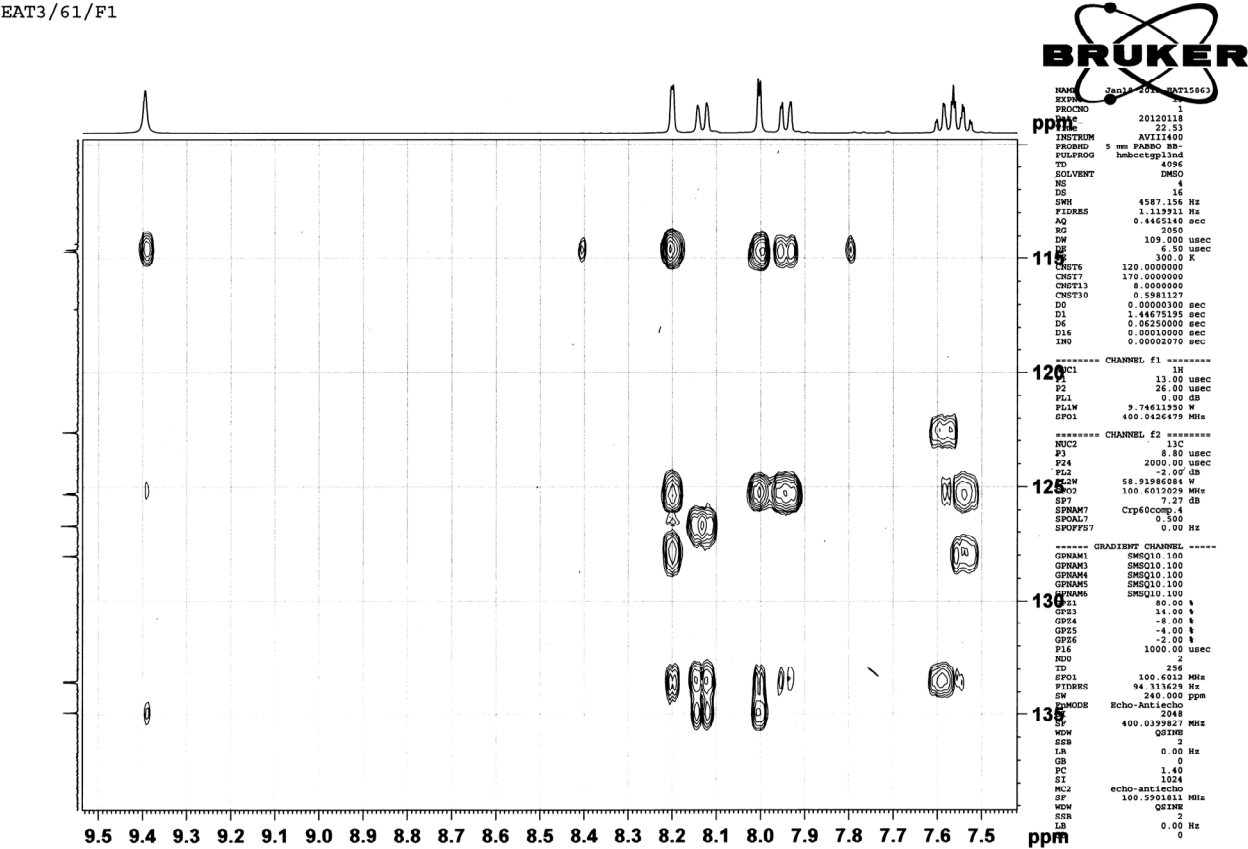
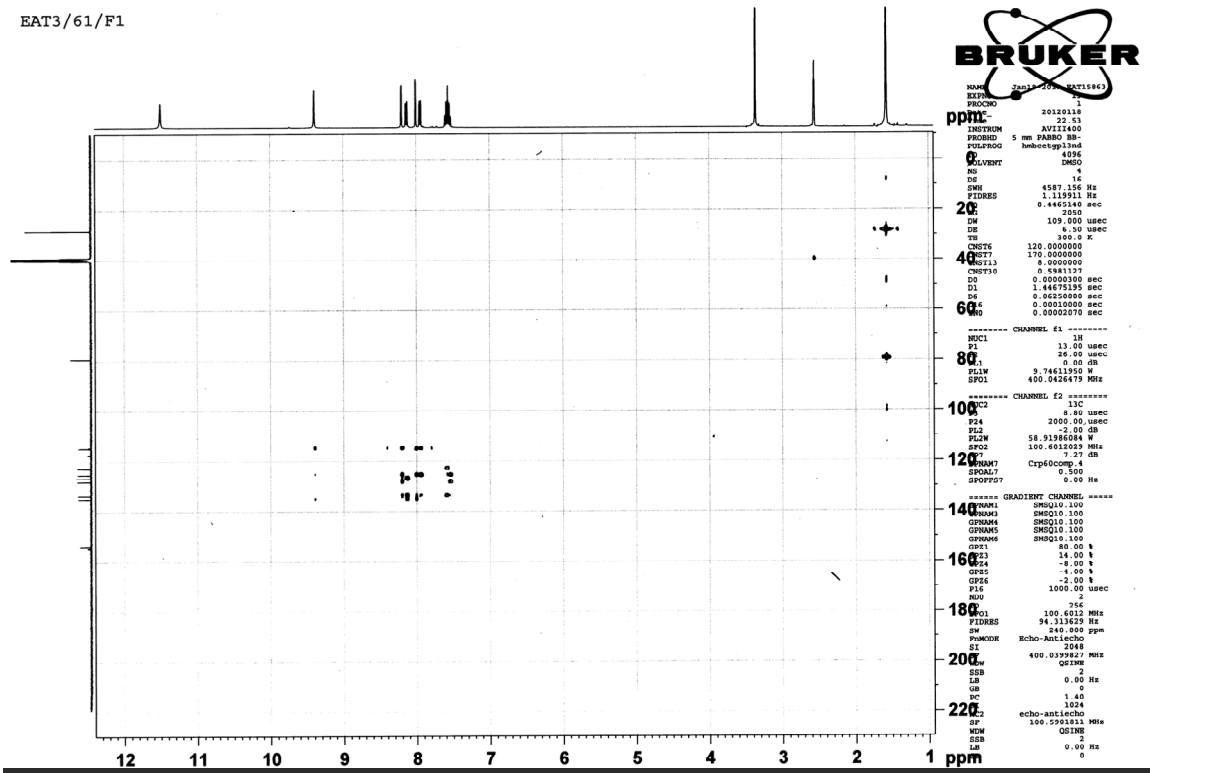


Figure 52. Expansion of part of  $^{13}\text{C}$  NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .





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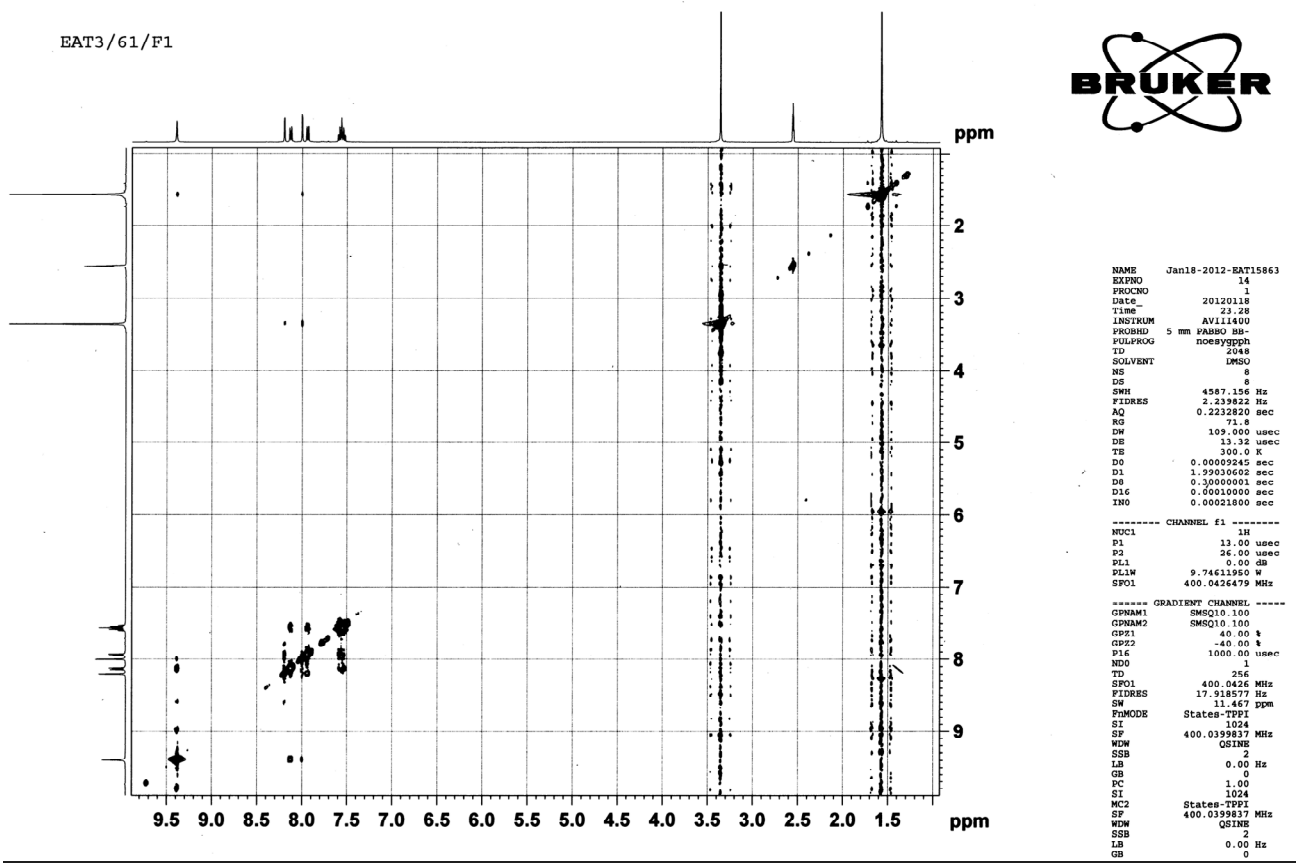


Figure 57.  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .

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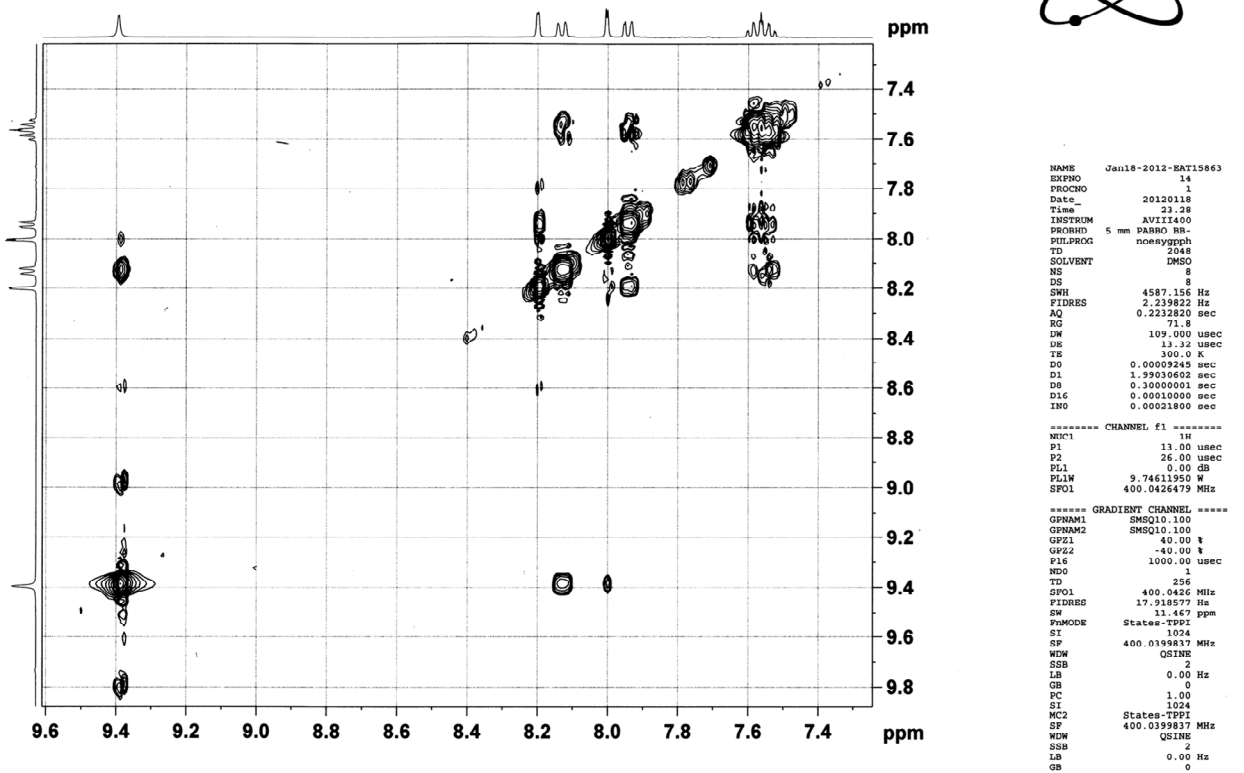
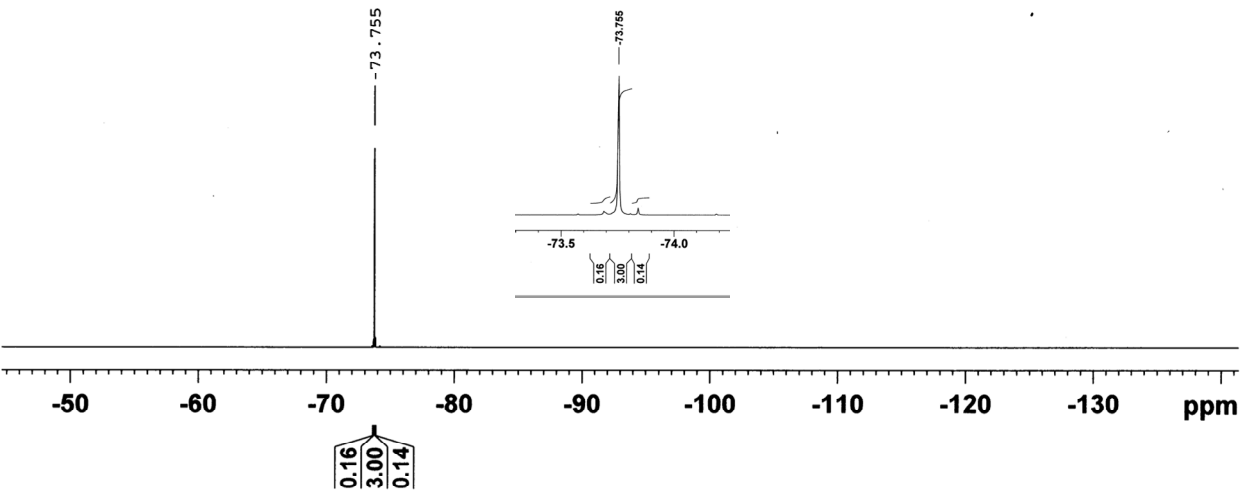
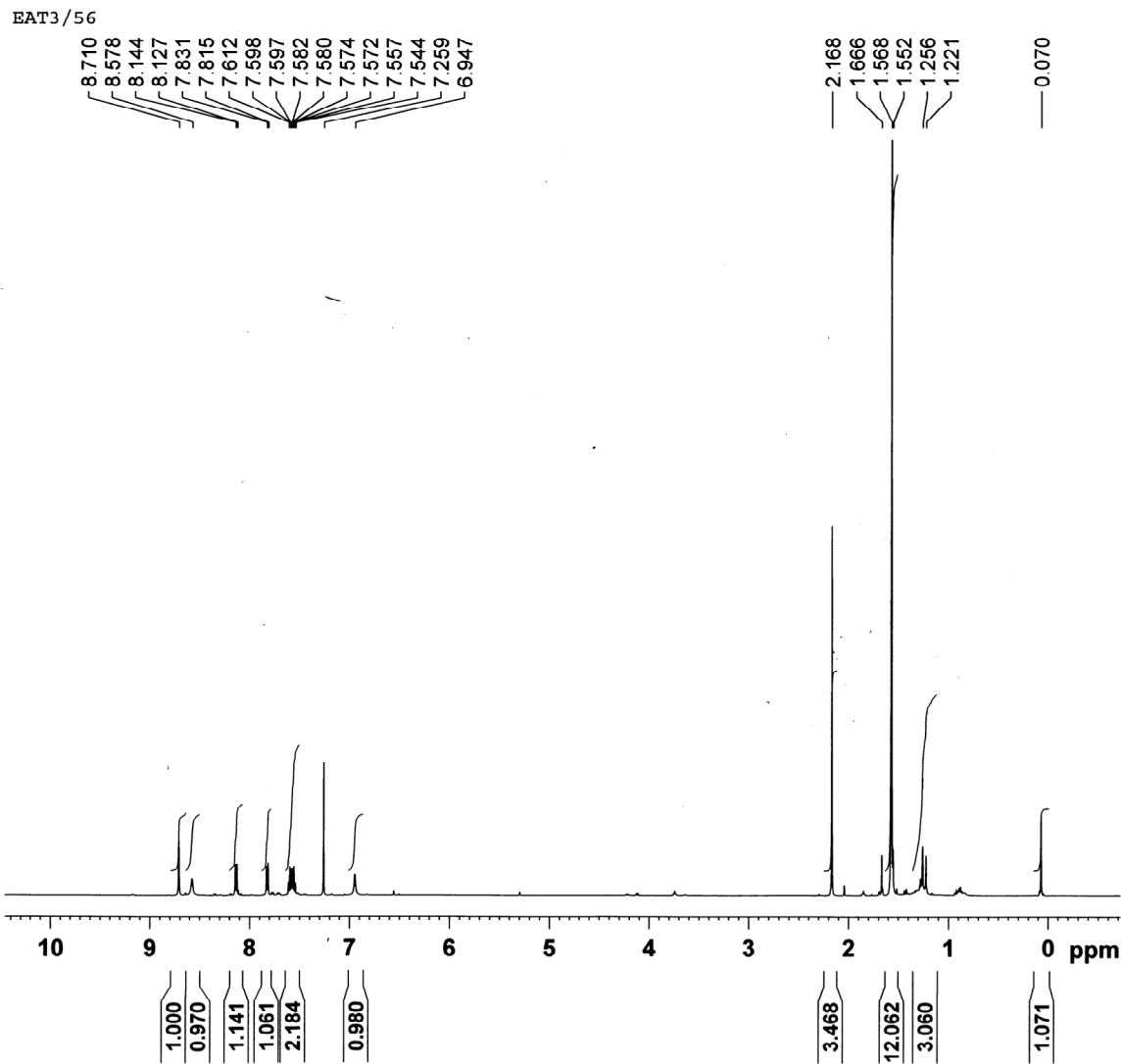


Figure 58. Expansion of part of  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .



**Figure 59.**  $^{19}\text{F}$  NMR spectrum of **25** in  $(\text{CD}_3)_2\text{SO}$ .



**Figure 60.**  $^1\text{H}$  NMR spectrum of **26** in  $\text{CDCl}_3$ .

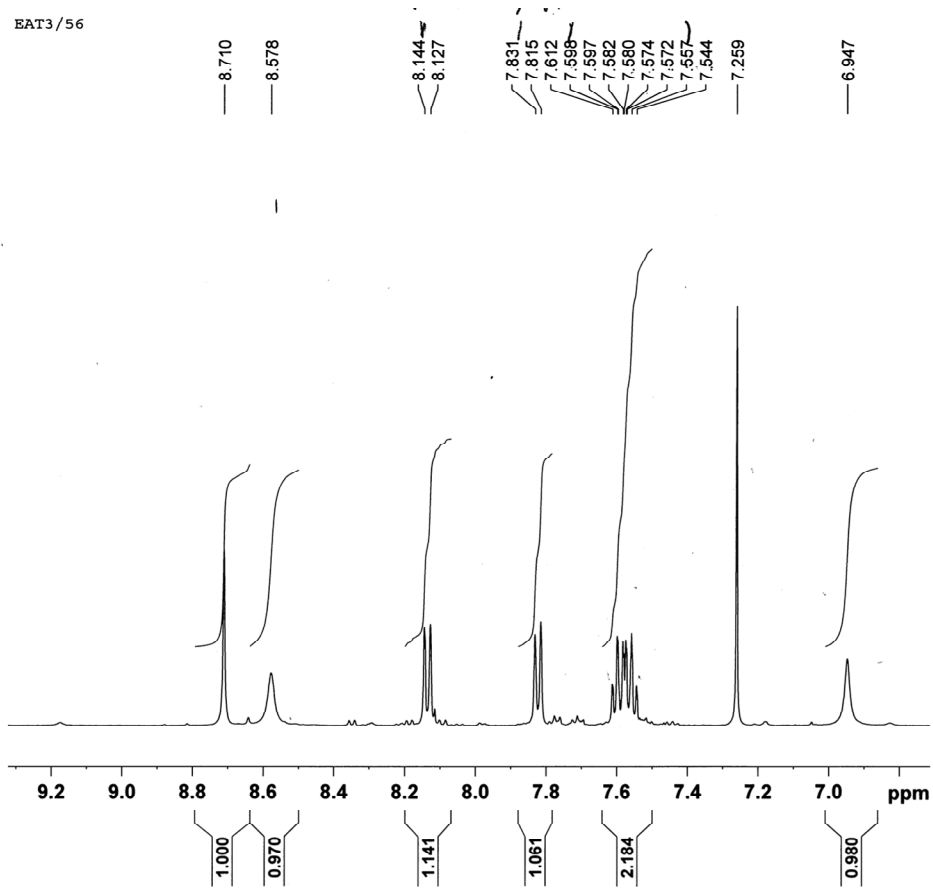


Figure 61. Expansion of part of  $^1\text{H}$  NMR spectrum of **26** in  $\text{CDCl}_3$ .

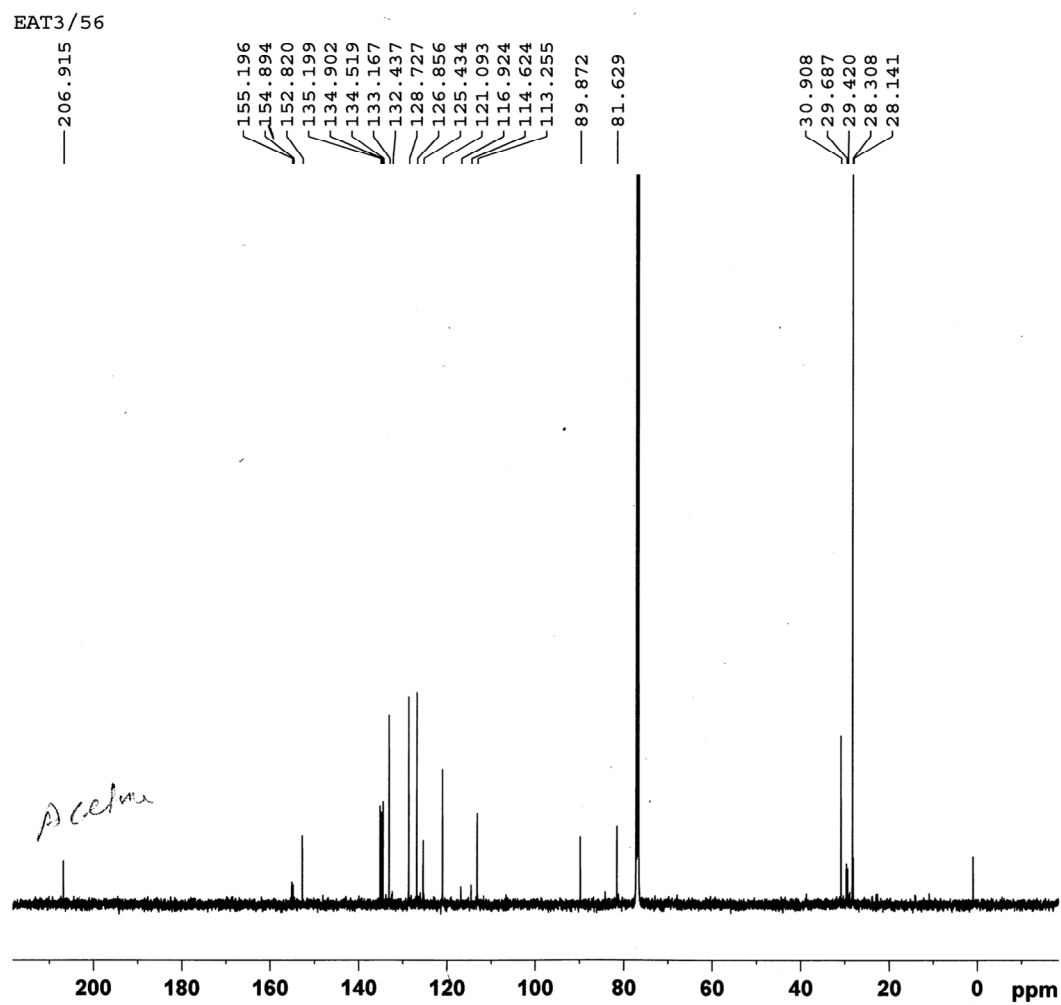


Figure 62.  $^{13}\text{C}$  NMR spectrum of **26** in  $\text{CDCl}_3$ .

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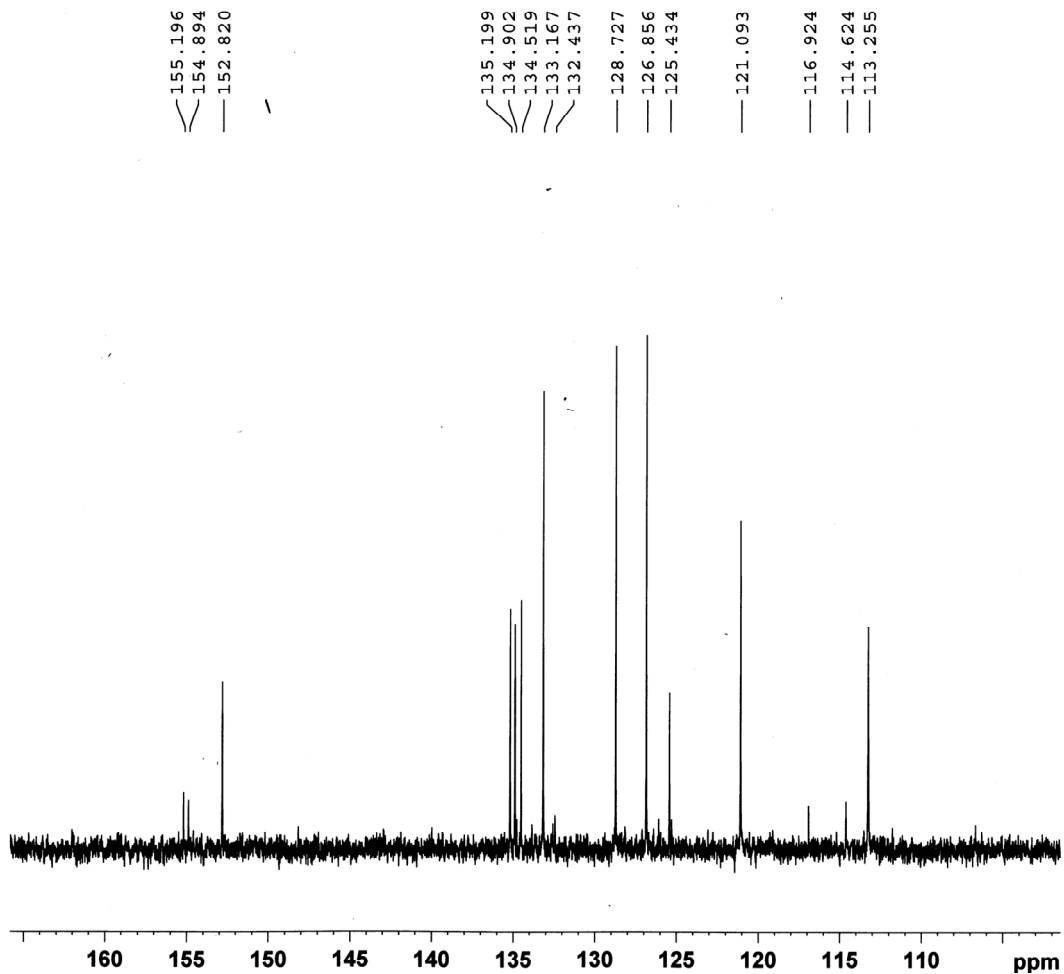


Figure 63. Expansion of part of  $^{13}\text{C}$  NMR spectrum of **26** in  $\text{CDCl}_3$ .

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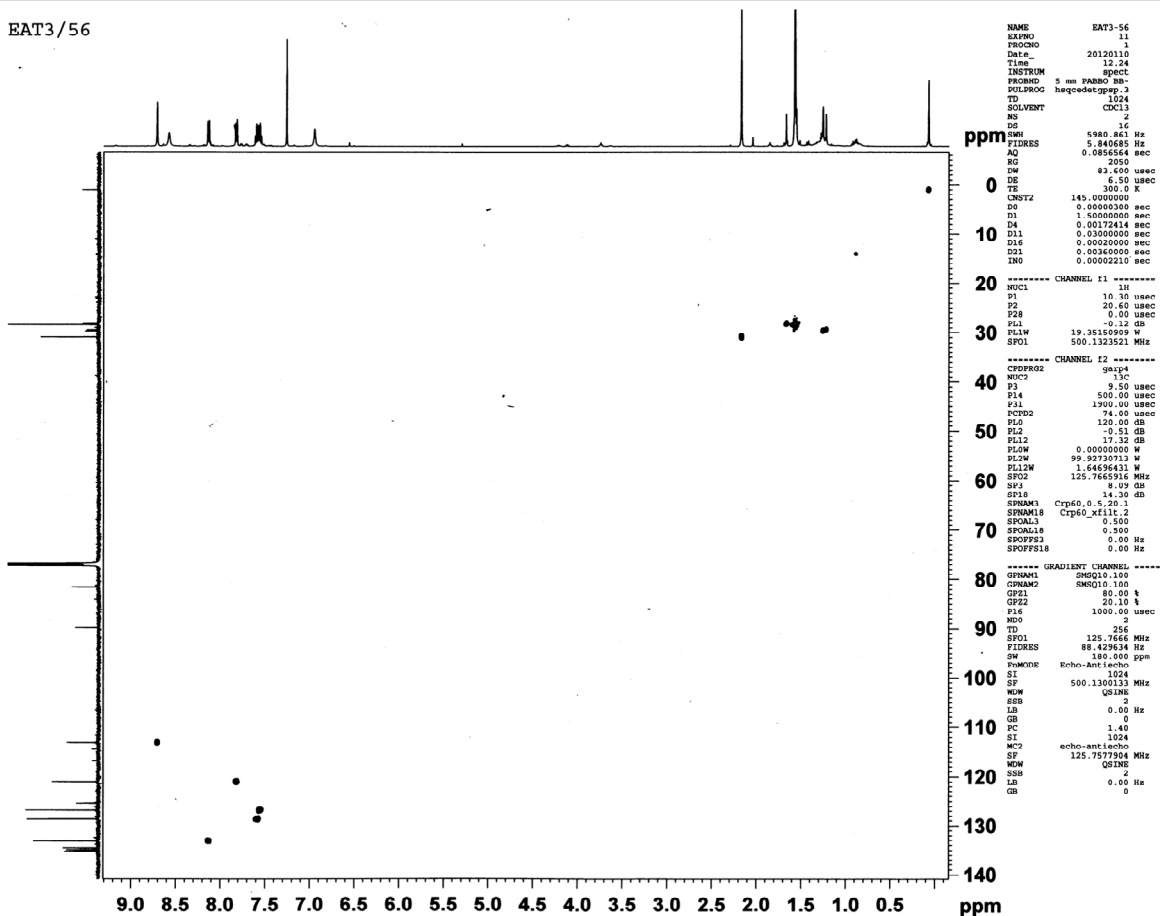


Figure 64. HSQC NMR spectrum of **26** in  $\text{CDCl}_3$ .

**Figure 66.** HMBC NMR spectrum of **26** in CDCl<sub>3</sub>.

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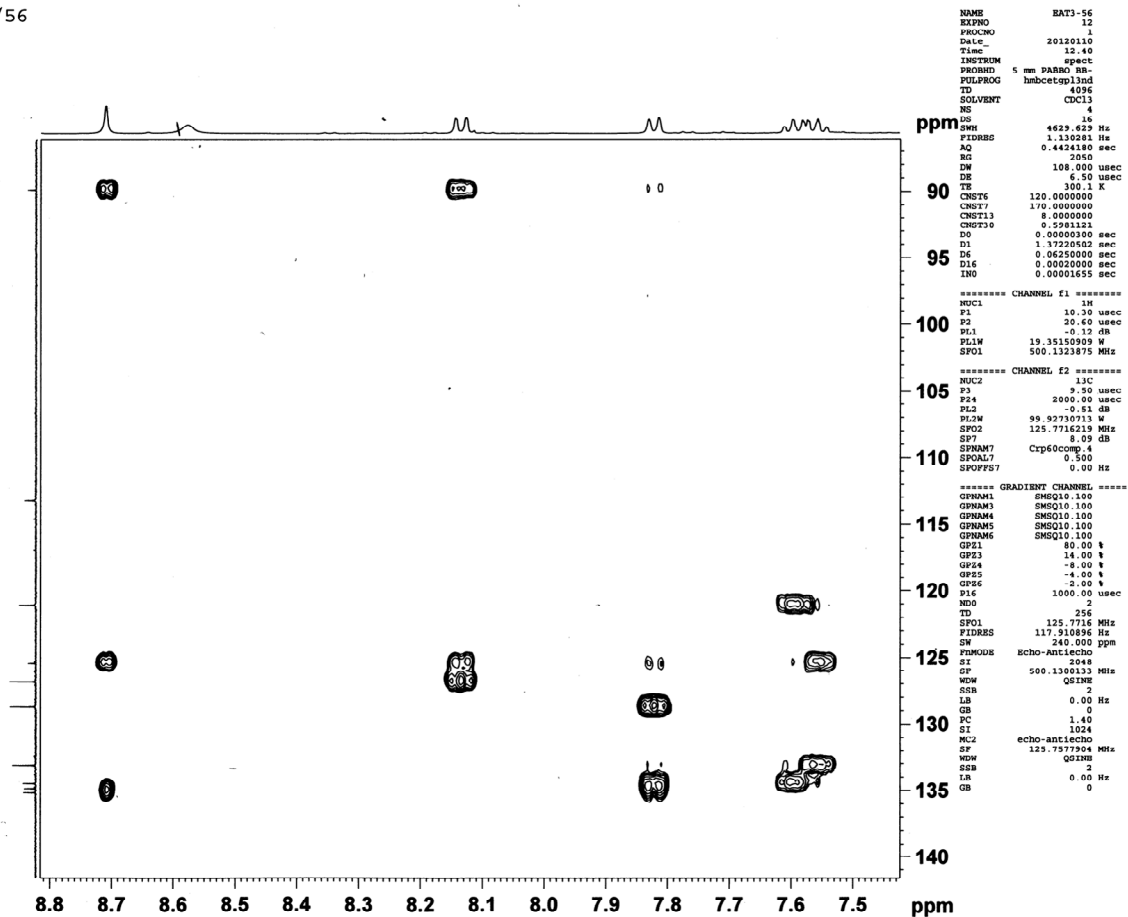


Figure 67. Expansion of part of HMBC NMR spectrum of **26** in CDCl<sub>3</sub>.

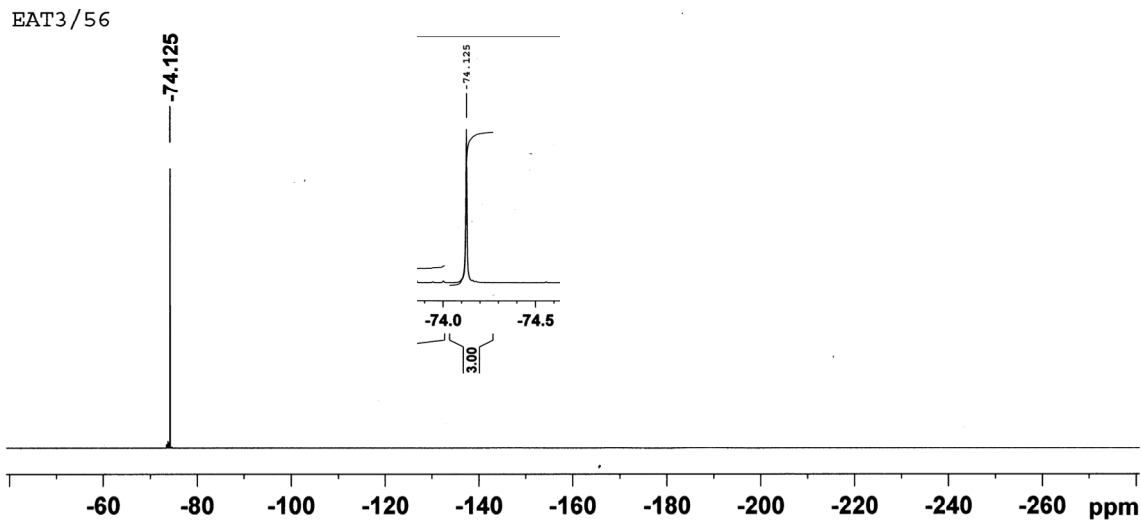


Figure 68. <sup>19</sup>F NMR spectrum of **26** in CDCl<sub>3</sub>.